

PHYSICAL-CHEMICAL
MECHANICS OF DISPERSE
SYSTEMS AND MATERIALS

PROGRESS IN
COLLOID AND INTERFACE SCIENCE

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Physical-Chemical Mechanics of Disperse Systems and Materials

Eugene D. Shchukin and Andrei S. Zelenev

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PHYSICAL-CHEMICAL MECHANICS OF DISPERSE SYSTEMS AND MATERIALS

Eugene D. Shchukin
Andrei S. Zelenev



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Contents

Foreword	ix
Preface.....	xi
Authors.....	xiii
Introduction.....	xv

SECTION I Coagulation Contacts and Structures

Chapter 1 Surface Forces and Contact Interactions.....	3
1.1 Physical-Chemical Phenomena at Interfaces	3
1.1.1 Three-Phase Contact Line: Wetting.....	8
1.1.2 Capillary Rise Method.....	12
1.1.3 Sessile Drop Method	12
1.1.4 Spinning Drop Method.....	13
1.1.5 Molecular Dynamics of Wetting	24
1.2 Thermodynamic Characteristics of a Contact between Particles.....	26
1.3 Contact Interactions between Solid Surfaces of Different Nature in Various Liquid Media.....	33
1.3.1 Methods Used to Measure Contact Forces.....	33
References	40
Chapter 2 Adsorption of Surfactants and Contact Interactions	43
2.1 Adsorption Phenomena at Interfaces.....	43
2.2 Mechanisms of Surfactant Behavior at Different Interfaces.....	55
2.3 Contact Interactions in the Presence of Surfactants: The Role of Surfactant Adsorption	60
2.3.1 Contacts between Cellulose Fibers: The Evaluation of Friction Forces and Contact Strength; the Effects of Common Papermaking Chemicals	64
References	72
Chapter 3 Coagulation Structures: Rheological Properties of Disperse Systems	75
3.1 Principles of Rheology	75
3.1.1 Main Rheological Models.....	75
3.1.1.1 Elastic Behavior.....	75
3.1.1.2 Viscous Flow	77
3.1.1.3 Plastic Flow (Plasticity).....	78
3.1.2 Combination of Rheological Models	80
3.2 Rheological Properties of Coagulation Structures.....	84
3.2.1 Mechanism of Elastic Aftereffect in Structured Dilute Suspensions of Bentonite.....	97
3.2.1.1 Elasticity Modulus	100
3.2.1.2 Viscosity of the Elastic Aftereffect	102
3.2.2 The Role of Contact Interactions in the Rheological Behavior of Fibrous Suspensions.....	105
References	109

Chapter 4	Contact Interactions and the Stability of Free-Disperse Systems.....	111
4.1	Key Factors Governing the Stability of Free-Disperse Systems.....	112
4.2	Rehinder's Lyophilic Structural–Mechanical Barrier as a Factor of Strong Colloid Stability.....	118
4.2.1	Stability of Fluorinated Systems: Strong Stabilization by the Structural–Mechanical Barrier	136
4.2.1.1	Rheological Properties of Interfacial Adsorption Layers in Fluorinated Systems	138
4.2.1.2	Study of the Rupture and Coalescence of Individual Droplets.....	139
4.2.1.3	Interactions between Hydrophobized Solid Surfaces in Nonpolar Liquids.....	141
4.3	Conditions of Spontaneous Dispersion and the Formation of Stable Colloid System.....	143
4.3.1	Behavior of $\Delta F(r)$ at $v = \text{const}$	146
4.3.2	Behavior of $\Delta F(n)$ at $r = \text{const}$	151
4.3.3	Behavior of $\Delta F(r)$ when $n = \text{const}$	154
4.3.4	Influence of the Interfacial Tension, σ , and Temperature, T , on ΔF	156
4.3.5	Concluding Remarks	157
4.3.6	Possibility of Obtaining Fine Disperse Structures in Melts by Hardening Melt Emulsions.....	159
4.4	Contact Interactions and the Stability of Sols Formed with Phases of Different Nature	162
	References	171

SECTION II *Surface Phenomena in the Structures with Phase Contacts and in Continuous Solid Bodies*

Chapter 5	Deformation and Degradation of Solid Bodies and Materials: Description and Measurements.....	177
5.1	Forces and Deformations in a Uniform Stressed State	177
5.1.1	Forces and Stresses.....	177
5.1.2	Strain, Displacements, and Turns.....	185
5.1.3	Elastic Deformations	189
5.1.4	Elastic Anisotropic Bodies.....	191
5.2	Heterogeneous Stressed State: Durability and Fatigue	193
5.2.1	Heterogeneous Stressed State.....	193
5.2.2	Concepts of Strength Theories.....	199
5.3	Mechanical Testing.....	203
5.3.1	Principles and Methods of Mechanical Testing	203
5.3.1.1	Some General Remarks	203
5.3.1.2	Static Testing Regime	204
5.3.1.3	Cyclic Fatigue Testing	209
5.3.1.4	Dynamic (Impact) Testing.....	210
5.4	Determination of the Structure–Rheological Characteristics.....	212
	References	221

Chapter 6	Structures with Phase Contacts.....	223
6.1	Phase Contacts between Particles in Disperse Structures.....	223
6.1.1	Effect of the Duration and Temperature of Ageing on the Size of Aluminosilicate Hydrogel Globules.....	232
6.2	Mechanisms of the Formation of Contacts and of the Development of Internal Stresses	235
6.2.1	Formation of Contacts between the Particles and the Development of Internal Stresses during the Hydration Hardening of Mineral Binders	236
6.2.1.1	Formation of Phase Contacts between Crystals of Gypsum	237
6.2.1.2	Effect of the Mutual Orientation of Crystals.....	241
6.2.1.3	Influence of the Compression Force	242
6.2.1.4	Bridging Crystals of Different Types	244
6.2.1.5	Effect of Chemical Modifiers and the Solution Composition on Crystallization Contacts.....	245
6.2.1.6	Bridging of Silica Particles.....	247
6.2.1.7	Investigation of the Microstresses in Disperse Structures Using X-Ray Diffraction	250
6.2.1.8	General Methodology of X-Ray Diffraction Studies.....	251
6.2.1.9	Internal Stresses in Structures Obtained in the Course of the Hydration Hardening of Various Binders.....	253
6.2.1.10	Stresses Formed in Structures Obtained by Pressing Powders.....	254
6.2.1.11	Dependence of Internal Stresses on the Conditions of the Hydration Hardening.....	254
6.2.1.12	Concluding Remarks on Hydration Hardening	256
	References	257
Chapter 7	Interfacial Phenomena in Processes of Deformation and Failure of Solids.....	259
7.1	Influence of an Active Medium on the Mechanical Properties of Solids: The Rehbinder Effect	260
7.1.1	Universal Nature and Selectivity of the Influence of the Medium on the Strength and Ductility of Solids with Different Types of Interatomic Interactions	261
7.1.1.1	Metals	264
7.1.1.2	Solids with Covalent Bonds.....	272
7.1.1.3	Solids with Ionic Bonds.....	274
7.1.1.4	Disperse Porous Materials.....	276
7.1.1.5	Organic Molecular Crystals.....	278
7.1.2	Role of the Actual Structure of the Solid and Role of External Conditions in the Manifestation of the Rehbinder Effect and the Deformation of Solids	282
7.1.2.1	Influence of the Real (Defect) Structure on the Adsorption-Induced Strength Lowering.....	283
7.1.2.2	Influence of Strain and Fracturing Conditions	288
7.1.2.3	Spontaneous Dispersion of Solids under Conditions of a Very Strong Reduction in the Free Interfacial Energy Facilitation of Mechanical Dispersion	299

7.1.2.4 Facilitation of Plastic Deformations in Solids under the Influence of an Adsorption-Active Medium 301

7.1.2.5 Numerical Modeling of the Rehbinder Effect 304

7.2 Influence of a Surface-Active Medium on the Mechanical Stability of the Surface of a Solid Surface Damageability 309

7.2.1 Lowering of the Strength of Glass Due to Microscopic Defects That Were Introduced to Its Surface 315

7.3 Rehbinder Effect in Nature and Technology 321

7.3.1 Physical-Chemical Mechanics of Catalysts: The Strength and Durability of Fine-Porous Materials in Active Media 325

7.3.1.1 Influence of Adsorption on the Mechanical Properties of Solids with Fine Porosity..... 329

7.3.1.2 The Effect of Catalysis on Mechanical Strength and Wear of Catalysts 333

References 341

Index..... 347

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Foreword

The authors of this book, Eugene D. Shchukin and Andrei S. Zelenev, represent the well-known Russian school of colloid and interface science, although both have been residing and working in the United States since the early 1990s. Dr. Shchukin has been a professor at Johns Hopkins University in Baltimore, Maryland, while continuing to teach and supervise research at the Colloid Chemistry Division at the Chemistry Department of Moscow State University, Moscow, Russia and at the Institute of Physical Chemistry of the Russian Academy of Science, Moscow, Russia. Dr. Zelenev has been pursuing a career as an industrial scientist holding a number of research and managerial positions with international chemical companies. This book is the authors' second joint project aimed at introducing the results and accomplishments of the Soviet and Russian school of colloid and interface science to the English-speaking audience.

Physical-chemical mechanics is a fundamental interdisciplinary area of science addressing the reciprocal effects of physical-chemical surface phenomena in disperse systems and materials and their mechanical behavior. Although it is based on colloid chemistry and material science, it is principally different from both of these disciplines. Colloid chemistry addresses the properties of matter in the dispersed state, and material science deals with properties of bulk materials. Conversely, physical-chemical mechanics is focused on the processes of transformation of disperse systems with a broad range of particle size from nanometers to millimeters into a material, as well as on the inverse processes of the transformation of materials into individual particles. The former takes place in various processes involving particle bridging, pressing, sintering, hydration hardening and sol-gel transitions, while the latter are encountered in material dispersion and failure by wear, friction, milling, various mechanical treatment, etc. The description of processes of material degradation and disintegration utilizes the principles and methods of material science as they apply to the description of mechanical strength. Although these two groups of processes are seemingly opposite to each other, they are united by the universal role of surface phenomena, such as adsorption of surface-active substances and media-induced lowering of interfacial free energy. These phenomena constitute a physical-chemical basis for the formation and healing of microscopic surfaces in the course of origination, development, and destruction of contacts between the particles. Contact interactions are the cornerstone subject of physical-chemical mechanics. Controlling contact interactions provides one with the means to influence numerous industrially important processes, such as those of increasing the strength of catalysts, drilling for oil and gas, papermaking, and many others.

Theoretical and experimental investigation of contact interactions is the leading theme of this book, while the chapters addressing the subjects of colloid and surface science and of material science are written with a level of detail that is necessary for understanding contact interactions and the transformation of individual particles into a material, and contrarily the conversion of a material into individual particles. Physical-chemical mechanics covers the broad spectrum of objects and systems, from milli- to nano-sized, and establishes the fundamental basis for controlling and tuning the properties of such systems and the processes taking place in them.

Physical-Chemical Mechanics of Disperse Systems and Materials contains seven chapters. Section I, with four chapters, presents the basics, starting from surface forces and the contact of particles with liquids. Chapter 2 is dedicated to adsorption phenomena, accumulation of surface-active molecules at various interfaces, and the importance of surfactant's adsorption on the contact between particles. The bulk properties of particle dispersions in liquids are discussed in Chapter 3 in terms of coagulation processes and the rheological behavior. Chapter 4 describes in a comprehensive way the stability of disperse systems and emphasizes the Reh binder effect as an important mechanism in stable colloidal systems. Section II consists of three chapters. Chapter 5 provides an introduction to the methodology of mechanical testing; Chapter 6 describes in detail the structures

with phase contacts, emphasizing numerous industrially important applications, such as hydration hardening of mineral binders; and Chapter 7 focuses on the essence and role of interfacial phenomena in the deformation and fracture of solids with different types of chemical bonding, with special attention to the role of active media, that is, on the Rebinder effect.

We are very happy that this book, unique in its topic and way of dealing with disperse systems and materials, is published as Volume 6 in the series Progress in Colloid Interface Science.

Reinhard Miller

Potsdam, Germany

Libero Liggieri

Genoa, Italy

Preface

This book provides a comprehensive description of physical-chemical mechanics, which is a discipline that uniquely bridges solid-state physics and materials science and colloid and surface chemistry. While colloid and surface science deals mainly with the *properties of a substance in a dispersed state*, and solid-state physics/material science are concerned mainly with the *properties of a substance making up a solid phase*, the scope of physical-chemical mechanics is different from the traditional studies of the properties of substances in that it consists of the investigation of complex *physical-chemical interfacial phenomena* taking place (1) in the course of the transition of a dispersed system into a material and/or, conversely, (2) in the course of the dispersion of a bulk material. This book is based on a critical assessment of results published in the literature, mostly in Russian, over the past four decades, and on the materials used in the lecture course on physical-chemical mechanics developed and taught by Professor Eugene D. Shchukin over many years at the Chemistry Department of Moscow State University in the USSR, and then in Russia, and at Johns Hopkins University in Baltimore, Maryland. The author has also taught the course on physical-chemical mechanics at the University of Sofia, Bulgaria, at Havana University in Cuba, at the Institute of Surface Chemistry (YKI) in Stockholm, Sweden, and at the Helsinki University of Technology in Finland. Many illustrations encountered throughout the book are based on the slides used in those lecture classes.

Professor Eugene D. Shchukin was a long-time collaborator and close friend of Professor Peter Alexandrovich Rehbinder (1898–1972), the founder of physical-chemical mechanics. Over many years, he worked closely with Rehbinder at the Laboratory of Physical-Chemical Mechanics at the Frumkin Institute of Physical Chemistry in Moscow and at the Chemistry Department of Lomonosov Moscow State University and continued to pursue active research in the area following Rehbinder's death. In the course of his work, Professor Shchukin has served as an advisor, co-advisor, and direct participant on numerous PhD and doctor of science thesis research projects. Some of the results presented in the book were generated as part of such thesis research. Those studies are not readily accessible to the English-speaking scientific community but are critical for understanding the underlying principles behind the formation of contacts and structures and common processes leading to wear, fracture, and failure, as well as the ambient media effects in these processes.

Since 1991, Professor Shchukin has resided in Baltimore, Maryland, where he has continued with his work in physical-chemical mechanics. The work conducted in Baltimore included the studies on contact interactions between cellulosic fibers in the presence of polyelectrolytes and surfactants, also included in this book. This was a joint project between Professor Eugene Shchukin, Dr. Igor Vidensky, and Dr. Andrei S. Zelenev, who is the second author of this book. Dr. Zelenev is a graduate of the Chemistry Department of Moscow State University and of Clarkson University (Potsdam, New York), where he earned his PhD in physical chemistry under the supervision of Professor Egon Matijević. Following graduation, Dr. Zelenev pursued a career in industrial research focusing on developing specialty chemicals for pulp and paper and later for oil and gas production. While belonging to the younger generation of scientists, Dr. Zelenev has a long history of collaboration with Professor Shchukin. The authors previously jointly coauthored the textbook *Colloid and Surface Chemistry* (Elsevier, 2001), which laid the path for preparing this book.

The present book is composed of the seven chapters that cover the material used as the basis for the lecture course on physical-chemical mechanics and basic material essential for understanding the content from the areas of colloid and surface chemistry, strength of materials, rheology, and tensors. Such coverage makes the book suitable for readers who do not have extensive knowledge and expertise in any of these areas. The book also devotes a lot of attention to the experimental methods used in physical-chemical mechanics and the relevant instruments, many of which were built and developed over the years by collaborators of Professor Shchukin. Where appropriate and

relevant, the authors have included a somewhat detailed description of specific significant studies. These studies are included in the corresponding chapters as essays. Some examples include studies on fluorinated systems, the damageability of glass, the strength of catalysts, etc. Dr. Andrei Zelenov has brought together and organized all of this very different material into a continuously flowing text. In order to maintain proper emphasis and the integrity of the presentation, the authors have occasionally used the same illustrations in different chapters.

The authors acknowledge the contribution from several critical participants of this project. They are indebted to Dr. Aksana M. Parfenova, who has prepared many others original illustrations used by Professor Shchukin in lecture classes. The authors also thank Harald Hille, a retired United Nations translator and terminologist, who read through the manuscript to check for infelicities in the English text, a language of which none of the authors is a native speaker, although they have worked as scientists in the United States for many years. Finally, the authors are indebted to Dr. Kristina D. Kitiachvili, who has provided invaluable help with the editing and prepublication organization of the manuscript.

Authors

Eugene D. Shchukin graduated in physics from Moscow State University (MSU, 1950) and earned a PhD (1958) and a doctor of science (1962) in physics and mathematics. The main positions he has held include the following: research professor at Johns Hopkins University (1994–2006) and professor emeritus (since 2006); professor (1967–2002), chairman (1973–1994), distinguished professor (since 1995) at the Colloid Chemistry Department at MSU, Institute of Physical Chemistry of the USSR Academy of Sciences, Head of Laboratory of Physical Chemistry Mechanics (1967–2003), and advisor (since 2003).

Dr. Shchukin's principal research interests are physical-chemical mechanics of disperse systems and materials, colloid and interface science, surfactant effects at various interfaces, stability of disperse systems, particles interactions and structure formation, materials science and engineering, physical chemistry of solid state, stability and damageability of solids and their surfaces in active media, control and applications in technology and environmental engineering.

He is a member of various Russian, U.S., and other international scientific committees and advisory and editorial boards. He was vice president of the International Association of Colloid and Interface Scientists during 1986–1988.

Dr. Shchukin was elected to the Russian Academy of Pedagogical Science (1965; recently Academy of Education), to the U.S. National (1984), Royal Swedish (1988), and USSR (1990, Russian) Engineering Academy; Founding Member of the Russian Academy of Natural Sciences (1990).

Dr. Shchukin is a recipient of the following prizes and awards: Lomonosov Prize from the MSU (1972), Lenin Prize from the Soviet Union (1988) (Equivalent to National Medal of Science in the United States), Reh binder's, Russian Academy of Sciences (1998), and a Gold Medal from the Russian Academy of Education (2008).

Andrei S. Zelenev graduated from the Department of Chemistry at Moscow State University, Moscow, Russia, (MSc, 1993), and from Clarkson University in Potsdam, New York (PhD, 1997). Since 1998, he has been working as an industrial scientist and researcher at Nalco Company (staff scientist) and CESI Chemical, a Flotek Company (research scientist and research manager), and currently with Fritz Industries (R&D manager, Stimulation).

Dr. Zelenev's professional interests include industrial applications of colloid and surface science, pulp and paper, oil and gas production, coagulation and flocculation, lyophobic and lyophilic colloidal systems, surfactant phase behavior, interaction of surfactants with surfaces, microencapsulation, particle deposition and aggregation, particle and surfactant transport in porous media, wetting and spreading, development of novel experimental methods for studying colloidal systems, and physical-chemical mechanics. Dr. Zelenev is an inventor on four issued U.S. patents and five pending patent applications, coauthor of 22 scientific publications, and coauthor of the textbook *Colloid and Surface Chemistry* (Elsevier, 2001).

Introduction

Looking at the title of this book, *Physical-Chemical Mechanics of Disperse Systems and Materials*, the first and very important question one might ask is what does it mean. Each of the six terms has a distinct and well-defined meaning, and together they define the scientific discipline originally introduced by Peter A. Rehbinder. The essence of physical-chemical mechanics is schematically illustrated by the chart shown in Figure I.1. Over many years, this chart was used by Professor Shchukin in lecture classes on the subject.

Let us try to understand which principal factors are the same for both disperse systems and the resulting materials.

First, there is the universal importance of mechanical properties defined in a broad sense as the ability of a material to resist mechanical action and the interest of both science and industry to control those properties. Depending on the need, one may seek to increase the resistance to mechanical action, thus ensuring strength and durability, or one may want to decrease that resistance in order to improve one's ability to form and machine a material.

Second, we deal with the real physical structure of a material, with the numerous defects associated with it, that is, micro- and ultra-micro-heterogeneity, defined by the connectivity between its many particles. Those connected particles form the basis for the structure. That implies that there is a universal nature of the disperse state with its highly developed internal and external surfaces.

Third, we consider the critical role played by various chemical and physical-chemical phenomena taking place at these surfaces and specifically the role of surface-active components present in the ambient medium.

Fourth, all of the *mechanical* processes of the deformation and fracture of a solid are of interest, and those involving the rupture and reformation of contacts between individual particles, as they constitute the processes of the rupture and restructuring of chemical bonds; that is, these are the *physical-chemical processes*.

Fifth, both disperse systems and the materials associated with them are united in the same cycle of transformations taking place in nature and technology. The universal nature of these mutual transitions is illustrated on the left-hand and right-hand squares shown in the diagram in Figure I.1 and reflect Rehbinder's principle of "achieving strength via damage."

The discussion of the transformation, rupture, and reformation of the bonds between the particles, and of the influence of the medium on these processes, constitutes the main subject of the first part of the book, which addresses structures with "weak" coagulation contacts between the particles, and the second part, which is devoted to the description of structures with "strong" phase contacts and of continuous materials. It would be useful to define these two broad classes of systems here.

Free-disperse systems are typically represented by dilute sols having low concentrations of particles, while the connected-disperse systems are those in which one typically encounters high particle concentrations, such as concentrated sediments or pastes (Figure I.2).

When the contacts between the particles in a free-disperse system are established, the transition of the system into a connected-disperse state takes place. This transition is associated with the development of a spatial network of particles in which the cohesive forces between the particles forming a network are sufficiently strong to resist thermal motion and the action of external forces. As a result of the transition, the system acquires a set of new structural-mechanical (rheological) properties that characterize the ability of the system to resist deformation and separation into individual parts. That is, the system acquires *mechanical strength*, which is the principal and universal characteristic of all solid and solid-like materials. For many materials, their mechanical strength defines the conditions of their use.

Although it may sound intuitively obvious that one would want to get durable and long-lasting materials, strength is not always the feature that is sought. Some examples where that is the case

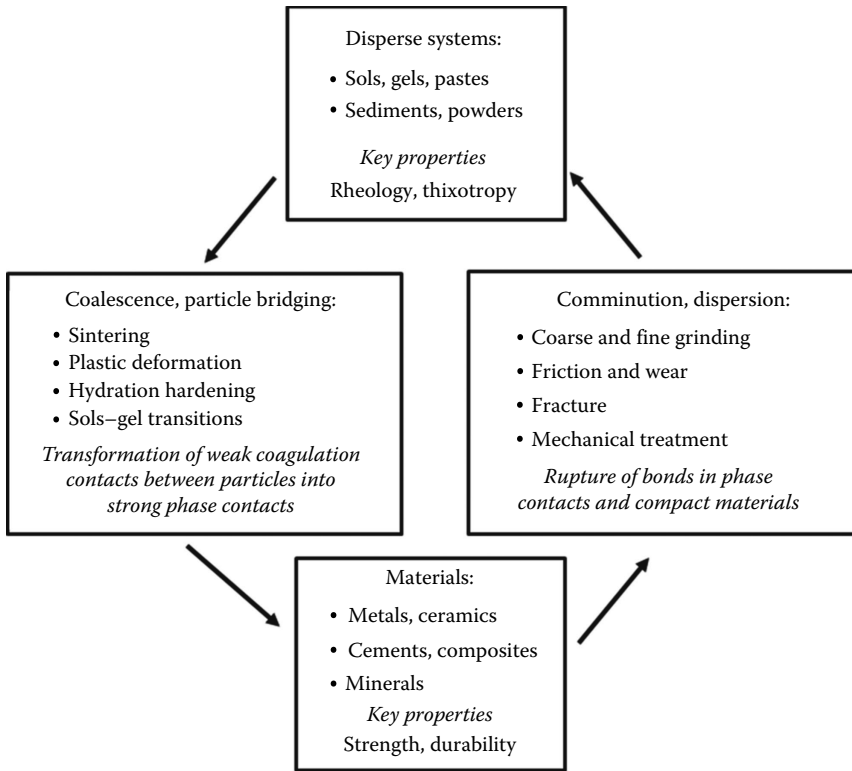


FIGURE 1.1 The main objects of physical-chemical mechanics and the relationships between them.

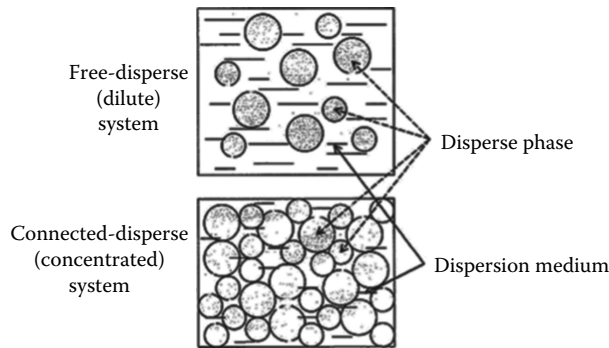


FIGURE 1.2 Free-disperse systems and connected disperse systems.

include various processes involving the formation of disperse systems, the packing of powders, the densification of suspensions or in the treatment of metals in the course of grinding, cutting, or pressing. In all of these applications, the main goal is to decrease mechanical resistance to treatment. At the same time, a decrease in strength may result from specific use conditions, and one needs to pay special attention to such factors in the numerous and dangerous processes of wear and failure in construction materials and the parts of various machines and mechanisms, etc. In order to seek ways to prevent and minimize potential damage, a good understanding of the underlying mechanisms is needed.

The understanding of structure formation in disperse systems, including the investigation of the mechanical properties of various structured systems, the optimal conditions for their formation,

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treatment, and fracturing (with a special emphasis on the role of active media), is one of the central subjects in the study of the physical-chemical mechanics of disperse systems and materials.

Physical-chemical mechanics originated in the 1930s and 1940s and in the 1950s became a separate and unique discipline bridging colloid and interface science with material science. Critical contributions to this area were made by various academic and industrial research groups working in the former USSR, specifically by scientists belonging to the scientific school established by Peter Alexandrovich Reh binder (1898–1972), the discoverer of the Reh binder effect. Numerous early and highly significant studies in the area conducted over the span of several decades are reviewed and referenced throughout the book.

Physical-chemical mechanics addresses a great variety of different objects and applications. These include various disperse systems, such as pastes, powders, and suspensions, encountered in various areas and applications; various materials used in modern technology; and such natural objects as minerals, soils, and bone tissue. This great variety emphasizes the universal nature of the disperse state of matter and the universal importance of mechanical properties.

Among the variety of disperse systems, fine disperse systems with particles in the range of 1–100 nm, commonly referred to as *nanosystems*, play an important role. Achieving a fine degree of dispersion and the highest possible uniformity is the prerequisite for obtaining strong and durable materials. At the same time, the high surface area of such materials provides for the highest effectiveness of various heterogeneous chemical processes involving mass and heat transfer.

The highest possible degree of dispersion cannot be achieved by simple comminution and grinding, that is, by dispersion processes. It can only be achieved by condensation methods. The latter involve the nucleation of a new phase in the initial homogeneous system at high levels of supersaturation.

Due to the large number of contacts between the particles, one encounters difficulties in stabilizing and molding fine disperse colloidal systems. The cohesive forces existing between the particles in such systems constitute the manifestation of physical-chemical interactions. By investigating the relationship that exists between the mechanical properties of disperse systems and materials, their structure, and interfacial phenomena, one seeks to find new ways to tune and control the properties of materials. This is achieved by using a controlled combination of mechanical action (including vibration) and physical-chemical means of controlling the interfacial phenomena—for example, by using surfactants.

Within the scope of physical-chemical mechanics, various approaches are used to describe the mechanical properties of various liquid-like and solid-like bodies and materials. These include the methods of macro- and microrheology, and molecular dynamic experiments, allowing one to approach the problem at the molecular dimension. The combination of these approaches provides one with the means to analyze the properties of real disperse systems and with methods for controlling them. Special attention is devoted to the Reh binder effect, that is, to the adsorption-related influence of the dispersion medium on the mechanical properties of solids.

The structure formation that takes place in disperse systems is the result of spontaneous, thermodynamically favorable processes of particle cohesion, leading to a decrease in the free energy of the system, such as particle coagulation or substance condensation at the points of particle contact. The development of spatial networks of various types is the foundation for the ability of a disperse system to transform into a material. As a result of such a transformation, the system acquires new characteristics and properties that are completely different from those in the original state.

Material strength, P_c (N/m), is the principal characteristic of a given material, determining the ability of a material to resist fracture under the action of external stresses. In disperse systems of *globular type* (Figure I.3), the strength P_c is determined by the combination of cohesive forces acting in the particle–particle contacts and the number of such contacts per unit area, that is,

$$P_c \approx \chi p_1$$

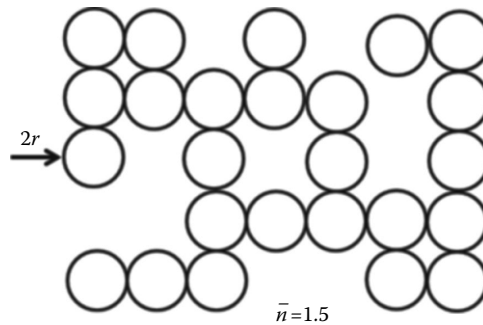


FIGURE I.3 The model of a globular disperse structure.

Both p_1 and χ can be obtained experimentally and estimated theoretically, as will be thoroughly discussed in the book.

The value of χ is determined by system geometry, primarily by the particle size (radius r , if the particles are spherical) and the particle packing density. In the case of moderately dense structures, such as those with a primitive cubic lattice with the coordination number of 6, one can approximately write that

$$\chi \approx \frac{1}{(2r)^2},$$

which provides one with the means to establish the spectrum of possible χ values in real systems. In particular, for $2r \approx 100 \mu\text{m}$, $\chi \sim 10^3\text{--}10^4$ contacts per cm^2 ; for $2r \approx 1 \mu\text{m}$, $\chi \sim 10^7\text{--}10^8$ contacts per cm^2 ; and for $2r \approx 10 \text{ nm}$, $\chi \sim 10^{11}\text{--}10^{12}$ contacts per cm^2 .

This description holds true for disperse systems of the globular type, in which a continuous backbone is formed due to the cohesion of the individual particles in the course of transformation of a free disperse system into a connected disperse system. In such systems, the backbone formed is the main carrier of the strength. At the same time, there are also other types of systems, for example, those with a cellular structure (solidified foams or emulsions). Such structures are typical in polymeric systems and may form in the course of new phase formations by condensation in mixtures of polymers. An individual approach also needs to be employed in the description of the mechanical properties of structures with anisometric particles, due to the specifics of the cohesive forces in such systems. In addition to porous structures, we also consider various compact microheterogeneous structures, such as mineral rocks, modern composite materials, and natural materials such as bone and wood.

Depending on the nature of the forces involved in the particle cohesion, the contacts can be subdivided into *coagulation contacts* and *phase contacts*, as schematically shown in Figure I.4. Coagulation contacts are discussed in detail in the first section of the book. In these contacts, particle–particle interactions are limited to direct “touching,” either directly, or via the remaining gaps filled with the dispersion medium (Figure I.4). The strength of the coagulation contacts is determined



FIGURE I.4 Contacts between particles: (a and b) coagulation and (c) phase.

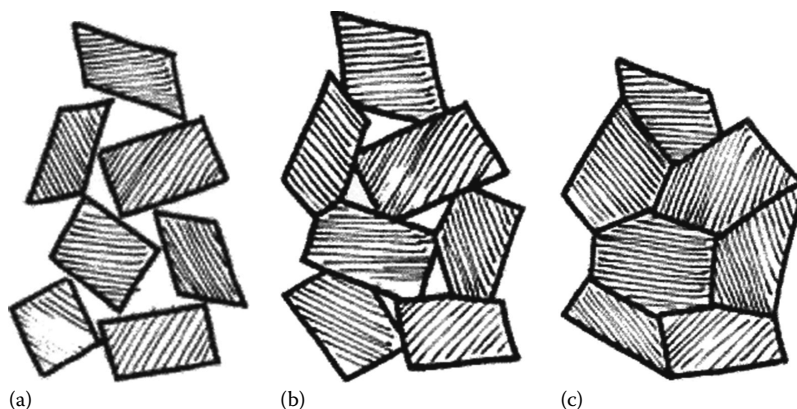


FIGURE I.5 Structures with (a) coagulation contacts, (b) phase contacts, and (c) a continuous body.

by the surface forces of the intermolecular interactions and for spherical particles with radii of 10 nm, 1 μm , and 1 mm, which is on the order of 10^{-9} – 10^{-10} , 10^{-7} – 10^{-8} , and 10^{-4} – 10^{-5} N, respectively.

Structures based on coagulation contacts (Figures I.4 and I.5) are typically characterized by low strength and mechanical reversibility manifested in their ability to spontaneously restore their previous structure after mechanical degradation (*thixotropy*, see Chapter 3).

The presence of an essentially similar liquid medium and of surfactant adsorption influences the magnitude and nature of the surface forces and may result in weakened cohesion in the contacts by two to three orders of magnitude. In a *lyophilized*, highly concentrated system in which the particles are brought into mechanical contact, this is revealed through lower resistance to deformation, τ^* , and results in a plasticizing of the system (see Chapters 2 and 3). When the disperse phase concentration is low, lyophilization leads to the preservation of the colloidal stability of a free-disperse system, that is, the resistance of the system to coagulation (see Chapter 4).

The second section of the book principally deals with different types of contacts—the so-called *phase contacts*. These contacts are substantially stronger than coagulation contacts and are mechanically irreversible. The transition from coagulation contacts to phase contacts corresponds to a transition from a simple “touching contact” (due to weak van der Waals forces) to the “accretion” of particles over a significant area (Figures I.4 and I.5). The accretion process is associated with the formation of a bridge of the new phase. This takes place in various processes involving the mutual plastic deformation of particles subjected to compressive forces, in sintering, the hydration hardening of mineral binders, and in sol-gel transitions.

In phase contacts, the cohesion between the particles is caused by short-range cohesion forces, which propagate over the area, significantly exceeding the dimensions of an elementary cell. There are about 10^2 – 10^3 interatomic bonds involved in the cohesion, and the contact surface may be compared to the region of a grain boundary in polycrystalline material. Once phase contact has been established, the transition from one bridged particle to the other can be accomplished within the same phase (Figure I.4), which is the reasoning behind the terminology.

For a large number of materials, the minimal value of the strength of such contacts is in the range between 10^{-8} and 10^{-6} N. As the area increases, the strength of the phase contacts also increases, reaching $\sim 10^{-4}$ – 10^{-3} . The strength of structures with phase contacts covers a range from 10^4 to 10^8 N/m² or even broader. In contrast to coagulation contacts, phase contacts are fractured irreversibly. Structures with phase contacts and the corresponding materials are discussed in detail in Chapter 6.

Consequently, we can see that physical-chemical mechanics is the interdisciplinary area of science that employs the principles and concepts of colloid and surface chemistry on the one hand and of physics and material science on the other.

At the same time, physical-chemical mechanics should not be viewed as a simple combination of particular fields of these areas of science. The main subject of colloid and surface chemistry concerns the properties of a substance in the disperse state, which is a microheterogeneous state characterized by highly developed interfaces. Material science and physics mainly address the properties of a substance in the state of a solid phase. This state is characterized by the absence of highly developed interfaces. Physical-chemical mechanics connects these two principally different areas by addressing the physical-chemical interfacial phenomena involved in the mutual transformation of a disperse system into a material, or in the conjugate processes of the dispersion of solids, rather than by focusing on the substance properties. Within the scope of physical-chemical mechanics, the general thermodynamic, kinetic, and structural regularities describing the formation of cohesive contacts or the onset of damage as principally surface phenomena are identified. Physical-chemical mechanics especially focuses on the determining role of initial surface defects in the origination and further development of damage in solids. The presence of the active components of the medium, of adsorption, or of contact with the related liquid phases may significantly influence the processes of particle cohesion or the formation of cracks. Depending on the conditions, the latter can be both facilitated and retarded. Among such physical-chemical processes studied by physical-chemical mechanics, special attention is devoted to the media-induced lowering of the strength of solids due to the lowering of surface energy, known as the *Rehbinder effect*, which is discussed in detail in Chapter 7.