COLLOIDAL SUSPENSION RHEOLOGY

Colloidal suspensions are encountered in a multitude of natural, biological, and industrially relevant products and processes. Understanding what affects the flow behavior, or rheology, of colloid suspensions, and how this flow behavior can be manipulated, is important for successful formulation of products such as paint, polymers, foods, and pharmaceuticals. This book is the first devoted to the study of colloidal rheology in all its aspects. With material presented in an introductory manner, and complex mathematical derivations kept to a minimum, the reader will gain a strong grasp of the basic principles of colloid science and rheology. Beginning with purely hydrodynamic effects, the contributions of Brownian motion and interparticle forces are covered, before the reader is guided through specific problem areas such as thixotropy and shear thickening; special classes of colloid suspensions are also treated. The techniques necessary for measuring colloidal suspension rheology are presented along with methods to correlate and interpret the results. An essential guide for academic and industrial researchers, this book is also ideal for graduate course use.

JAN MEWIS is Emeritus Professor of the Chemical Engineering Department at the Katholieke Universiteit Leuven. He is involved in industrial and academic research in complex fluids such as suspensions and polymer blends. Professor Mewis has lectured all over the world and has written over 200 publications on colloid science and rheology. He was Chairman of the International Committee on Rheology and is a recipient of the Gold Medal of the British Society of Rheology and the Bingham Medal of The Society of Rheology (USA).

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To Ria and Sabine

This landmark book thoroughly details the basic principles of colloid science and uniquely covers all aspects of the rheology of colloidal suspensions, including difficult and often controversial topics such as yield stress, thixotropy, shape effects and shear thickening, as well as latest developments in microrheology and interfacial rheology. The elegant presentation style, focusing on the fundamental concepts, bridging engineering and physics, experiment and theory, and paying attention to the interplay between microstructure and rheology, reflects the vast teaching and research experience of the authors, and makes the book a much needed reference for practitioners, researchers and graduate students.
Dimitris Vlassopoulos
IESL-FORTH, Greece

Appropriately, the first book to span the subject of suspension rheology is authored by Jan Mewis, a pioneer in the field, and Norm Wagner, whose research has advanced many of the modern frontiers. Their text emerges from a long-standing collaboration in short courses that have introduced graduate students, young faculty, and industrial researchers to the fundamentals and the practicalities of rheological phenomena and their underlying principles. After a brief introduction to colloid science and rheology the book teaches the consequences of the relevant forces, i.e., hydrodynamic, Brownian, electrostatic, polymeric, and van der Waals, through data from model systems and results from fundamental theory. Then time-dependent phenomena, shear thickening, and the effects of viscoelastic media, in which the two have paved the way, receive special attention. The treatment closes with brief accounts of microrheology, electro- and magnetorheology, and two-dimensional suspensions. There is much to learn from this tome!
William B Russel
Princeton University

Ever since I learned that Mewis and Wagner were preparing *Colloidal Suspension Rheology* I have been eagerly awaiting its arrival. I was not disappointed! The book is very logically laid out. The reader is told what is coming and key ideas are summarized at the end of every section. I especially like the “landmark observations” that focus each chapter. Every chapter has a table of notation and is extensively referenced including titles of articles. The concise review of colloidal phenomena in chapter 1 is outstanding and the Advanced Topics in the final chapter (microrheology, electro and magneto-rheology and 2 dimensional rheology) are a special treat.

Colloid Suspension Rheology is the first text in this field and will be much appreciated. Suspensions are growing rapidly in academic importance and are the key to so many new industrial products. Rheology is a rapid and sensitive tool to characterize both their microstructure and performance. This text will be of great excellent supplement to courses in colloids and rheology.
Chris Macosko
University of Minnesota & IPRIME

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Preface

Colloidal dispersions played an important role in the early history of rheology as it evolved into a defined branch of science and engineering. Bingham's model for yield stress fluids was based on experiments on dispersions, namely oil paints. About the same time, systematic measurements on colloidal systems were performed in Europe, especially in Freundlich's laboratory in Berlin. This work culminated in one of the first books on rheology: *Thixotropie* (Paris, 1935). In the subsequent decades the interest in rheology gradually shifted to polymers and the theory of viscoelasticity.

Understanding Brownian motion and its consequences motivated Einstein's work on intrinsic viscosity and von Smoluchowski's study of colloidal aggregation nearly a century ago. However, it was not until the theoretical work of G. K. Batchelor in the early 1970s that a full micromechanical framework for colloidal suspension rheology combining statistical mechanics and hydrodynamics existed. This stimulated much important work and since then the number of researchers and the progress of our understanding of the subject has increased dramatically. The result is a rapidly growing body of scientific and technical papers – experimental and theoretical work as well as simulations – contributed by chemists, physicists, biologists, and engineers alike.

Whereas there is a vast and expanding literature, there are no sources that provide a systematic introduction to the field. The growing number of newcomers to the field have available to them numerous textbooks on rheology and many more on colloid science, as well as specialized overviews in the research literature, yet no book with the sole focus on colloidal suspension rheology. Interest in the rheology of colloidal dispersions is not restricted to academia. Increasingly, the available knowledge is being applied effectively to solve formulation and processing problems, e.g., for coatings, inks, filled polymers and nanocomposites, metal and ceramic slurries, cement and concrete, mine tailings, drilling muds, pharmaceuticals, and consumer products. The lack of a basic text dedicated to this subject stimulated the writing of the present book, which is intended as a general introduction to colloidal suspension rheology for a beginner in the field. Its purpose is to provide a systematic overview of the established, central elements of the field. Practical examples are presented and discussed within a framework for understanding the underlying structure-property relationships. Emphasis is on understanding the various phenomena that contribute to the rheological properties of colloidal suspensions, such as available relations and scaling laws, as well as on the underlying micromechanical explanations. It is our intention that the micromechanical understanding of the model systems presented herein can assist in the formulation and investigation of systems of specific or practical interest to the reader. To that end, basic theoretical results are presented, but without mathematical derivation. Extensive references guide the reader to more detailed and advanced information.

The book starts with a brief introduction to basic concepts of colloid science and rheology as the bare necessities for those without prior knowledge of these disciplines and as a review and establishment of nomenclature useful for those already familiar with the subjects. The systematic study of colloid rheology begins with hydrodynamic effects. These are always present in dispersions and are the dominant contribution to the rheology of suspensions with large, non-colloidal particles (Chapter 2). The rheology of colloidal suspensions with increasing levels of complexity is treated systematically in the following chapters. Chapter 3 explores hard sphere dispersions, where Brownian motion is included and its effects analyzed. Next, repulsive interparticle forces are added to give colloidally stable systems (Chapter 4). Special features arising because of non-spherical particle shapes are discussed in Chapter 5. Chapter 6 examines the effects of attractive interparticle forces, leading to more complex microstructures, phase behavior, and thus rheology. Important time-dependent effects, such as thixotropy, are treated explicitly in Chapter 7. Chapter 8 is dedicated to the important phenomenon of shear thickening. Discussion of the rheological properties of colloidal dispersions is not complete without also covering specific problems related to accurate and precise rheological measurement, as well as the design of effective rheological experiments; this is the subject of Chapter 9. Whereas in all these chapters the suspending medium is assumed to be a Newtonian fluid, Chapter 10 considers the effects of suspending particles in viscoelastic media, covering the important cases of filled polymer solutions and melts and nanocomposites. The final chapter (11) provides a brief introduction to some advanced topics in suspension rheology, including sections on some special colloidal systems, more specifically electro- and magneto-rheological systems and colloids at interfaces: the so-called 2D dispersions. The latter section includes contributions by Professor J. Vermant (Katholieke Universiteit Leuven). In addition, some special rheological techniques are discussed, such as large amplitude oscillatory shear, superposition measurements, and microrheology, the latter section contributed by Professor E. Furst (University of Delaware). We thank these two colleagues for their valuable contributions to this text.

This book owes much to the scholarship of Professors W. B. Russel, W. R. Schowalter and the late D. A. Saville, all of Princeton University (and authors of *Colloidal Dispersions*), as well as the late Professor A. B. Metzner of the University of Delaware. It is through the schools of colloid science and rheology established at Princeton and Delaware that we became acquainted and started our research collaborations – their scholarship and mentoring motivated and influenced much of the science presented herein. Our many colleagues and mentors in the rheology community are also gratefully acknowledged. We thank Professors D. T. Leighton (University of Notre Dame), J. Morris (The City University of New York), D. Klingenberg (University of Wisconsin), J. Vermant (Katholieke Universiteit Leuven), and W. B. Russel for commenting on early drafts of some chapters. Many colleagues, co-authors, and especially former and current students provided us with very valuable suggestions and information for the book – although all of their names cannot be mentioned here, one can readily find their work presented and cited throughout the text. For help in preparing the figures we thank J. Coffman, D. Kalman, A. Eberle, A. Golematis, E. Hermans, N. Reddy, and A. Schott, as well as the many students at Delaware who commented on and helped proofread versions of the text.

Many funding agencies helped support our research in this area during the time we wrote the manuscript, including the US National Science Foundation, the International Fine Particle Research Institute, the US Army Research Office, and corporations including Kodak, DuPont, Unilever, and Proctor & Gamble. The presentation of materials has benefitted from the short courses we developed and taught for the US Society of Rheology, as well as other institutions around the world. We especially thank the University of Delaware and Katholieke Universiteit Leuven for supporting us and our collaborations over the years, which made this book possible.

We sincerely hope you enjoy reading this book as much as we have enjoyed writing it. Our experience continues to be that the growing fields of colloid science and rheology are not only intellectually stimulating but of significant practical importance. We find these fields to be particularly collegial, and the participants have been very helpful as we have selected and assembled materials. Space limitations necessitated omitting many fine examples of colloidal suspension rheology and associated phenomena, but we hope the extensive referencing will aid the reader in exploration beyond what we could present here.

General list of symbols

a	particle radius [m]
a_i	particle radius of species/size i [m]
A	Hamaker constant [J]
c	mass concentration [kg m^{-3}]
$\mathbf{D}$	rate-of-strain tensor [s^{-1}]
D_f	fractal dimension [-]
D_{ij}	components of the rate-of-strain tensor [s^{-1}]
$\mathcal{D}$	diffusivity tensor [m^2 s^{-1}]
$\mathcal{D}_0$	Stokes-Einstein-Sutherland diffusivity, Eq. (1.5) [m^2 s^{-1}]
$\mathcal{D}_{ij}$	components of the diffusivity tensor [m^2 s^{-1}]
$\mathcal{D}_r$	rotational diffusivity [s^{-1}]
$\mathcal{D}_{r,0}$	limiting rotational diffusivity for zero volume fraction [s^{-1}]
$\mathcal{D}^s$	self-diffusivity tensor [m^2 s^{-1}]
$\mathcal{D}^s_{ij}$	components of the self-diffusivity tensor [m^2 s^{-1}]
$\mathcal{D}^{ss}$	short-time self-diffusion coefficient [m^2 s^{-1}]
E	elasticity modulus [Pa]
e	electronic charge [C]
F	force [N]
g	gravity or acceleration constant [m s^{-2}]
$g(r)$	radial distribution function [-]
G	modulus [N m^{-2}]
G'	storage modulus [N m^{-2}]
G''	loss modulus [N m^{-2}]
G_{pl}	plateau modulus [N m^{-2}]
h	surface-to-surface distance between particles [m]
$\mathbf{I}$	unit tensor [-]
k	coefficient in the power law model [N s^n m^{-1}]
k'	coefficient in the Cross equation, Eq. (1.35) [s]
k_B	Boltzmann's constant [J K^{-1}]
k_H	Huggins coefficient [-]
L	length [m]
m	power law index in Cross model [-]
n	number density [m^{-3}]
N	number of particles [-]

N_A	Avogadro's number [mol^{-1}]
N_i	ith normal stress difference [Pa]
P	pressure [Pa]
P_y	compressive yield stress [Pa]
q	scattering vector [nm^{-1}]
R	radius [m]
R_g	radius of gyration [m]
r	distance from center of particle [m]
S	entropy [J K^{-1}]
t	time [s]
T	temperature [K]
U	relative velocity between particles [m s^{-1}]
v	local speed [m s^{-1}]
V	volume [m^3]
$\boldsymbol{v}$	velocity vector [m]
v_i	velocity component in the i direction, $i = x, y$, or z [m s^{-1}]
W	stability ratio [-]
W^{shear}	stability ratio for shear-induced cluster formation [-]
x	Cartesian coordinate, in simple shear flow the flow direction [m]
y	Cartesian coordinate, in simple shear flow the velocity gradient direction [m]
z	Cartesian coordinate, in simple shear flow the vorticity direction [m]
II_i	second invariant of tensor i

Greek symbols

γ	strain [-]
γ_0	peak strain [-]
$\dot{\gamma}$	shear rate [s^{-1}]
δ	phase angle [-]
Δ	half width of a square-well potential [m]
ε	dielectric constant [-]
ε	depth of a square-well potential [J]
ε_o	permittivity of vacuum [8.85×10^{-12} F m^{-1}]
η	(suspension) viscosity [Pa s]
η'	dynamic viscosity [Pa s]
$[\eta]$	intrinsic viscosity [cm^3 g^{-1}]
$[\eta]'$	dimensionless intrinsic viscosity [-]
κ	Debye-Hückel constant [m]
ν	number of particles or molecules per volume [m^{-3}]
Π	osmotic pressure [Pa]
θ	polar coordinate [-]
ρ	density [kg m^{-3}]
$\boldsymbol{\sigma}$	shear stress tensor [Pa]

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More Information

σ	shear stress in simple shear flow [Pa]
σ_y	yield stress [Pa]
σ_y^B	Bingham yield stress [Pa]
σ_y^d	dynamic yield stress [Pa]
τ	relaxation time [s]
τ_B	Baxter stickiness parameter [-]
ϕ	particle volume fraction [-]
Φ	particle interaction potential [J]
Ψ_i	ith normal stress coefficient [Pa s^2]
ψ	electrostatic potential [V]
Ψ	dimensionless electrostatic potential [-]
ψ_s	surface potential [V]
Ψ_s	dimensionless surface potential [-]
ζ	zeta potential [V]
ω	frequency [rad s^{-1}]
Ω	rotational speed [s^{-1}]

Subscripts

eff	effective
el	elastic contribution
ext	extensional
floc	*floc*
g	glass
gel	gel
lin	linearity limit
m	suspending medium/mean value
M	Maxwell
max	maximum value
p	particle
pl	plastic
r	relative
y	yield condition
0	limiting value in the zero shear limit
∞	limiting value at high shear rate or frequency

Superscripts

B	Brownian, with yield stress Bingham
C	Casson
d	dispersion
g	gravity
h	hydrodynamic
hcY	hard core Yukawa (potential)

hs	hard sphere
H	Herschel-Bulkley
I	interparticle contribution
m	power law index in Cross model
n	power law index for shear stress
s	surface
*	complex

Dimensionless numbers

Bo	Boussinesq number, Eq. (11.22)
De	Deborah number (ratio of characteristic material time to characteristic process time)
Ha	Hartmann number, Eq. (4.2)
Mn	Mason number, Eq. (11.13)
Mn_{mag}	magnetic Mason number, Eq. (11.17)
Pe_D	Péclet number for microrheology, Eq. (11.6)
Pe_i	Péclet number for the ions, Eq. (4.3)
Pe_μ	Péclet number for microrheology, Eq. (11.3)
Re	Reynolds number ($\rho V D/\eta$)
Re_p	particle Reynolds number ($\rho\dot{\gamma}a^2/\eta_m$), Eq. (2.11)
St	Stokes number ($m_p\dot{\gamma}/6\pi\eta_m a$)
Wi	Weissenberg number (N_1/σ)

Useful physical constants and values

Note that many CODATA internationally recommended values can be found at physics.nist.gov/cuu/Constants/.

Constant		Value
e	Elementary charge	$1.602\,176\,487 \times 10^{-19}$ C
g	Standard acceleration of gravity	$9.806\,65$ m s^{-2}
k_B	Boltzmann's constant	$1.380\,650\,4 \times 10^{-23}$ J K^{-1}
m_u	Atomic mass unit	$1.660\,538\,782 \times 10^{-27}$ kg
N_A	Avogadro's number	$6.022\,214\,170 \times 10^{23}$ mol^{-1}
R	molar gas constant	$8.314\,472$ J mol^{-1} K^{-1}
ε_0	Electric permittivity of vacuum	$8.854\,187\,817 \times 10^{-12}$ C^2 N^{-1} m^{-2} [F m^{-1}]
μ_0	Vacuum permeability	$4\pi \times 10^{-7}$ N A^{-2}

Characteristic values

k_BT	4.1×10^{-21} J (at room temperature)
k_BT/e	25.7 mV (at room temperature)
κ^{-1}	3.08 nm for a 10 mM 1:1 electrolyte in water at room temperature
l_b	0.7 nm for water at room temperature
Q	typically of $\mathcal{O}(1)$ μC cm^{-2}

Properties of water at 298 K

ε	relative dielectric constant	80
η	viscosity	8.90×10^{-4} Pa s
ρ	density	997 kg m^{-3}

Useful Hamaker constants in water (units of 10^{-20} J)

Decane	0.46
Fused silica	0.85
Gold	30
Polystyrene	1.3
Poly(methyl methacrylate)	1.05
Poly(tetrafluroethylene)	0.33