RHEOMETRY OF PASTES, SUSPENSIONS, AND GRANULAR MATERIALS

Applications in Industry and Environment

Philippe Coussot

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data:

Coussot, Philippe.
Rheometry of pastes, suspensions, and granular materials : applications in industry and environment / Philippe Coussot.
p. cm.
Includes index.
ISBN 13 978-0-471-65369-1
ISBN 10 0-471-65369-1
1. Amorphous substances. 2. Rheology. I. Title.
TA418.9.A58C68 2005
620.1′1—dc22 2004021908

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

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PREFACE

Although the behavior of clays and paints initially prompted Bingham [1] to introduce rheology as a new scientific field in the early 1920s, the main developments in that field since then have concerned polymers. The internal structure of polymers can now be easily characterized using various techniques and shows obvious physical similarities between materials. As a consequence, a general descriptive framework for these materials is available now, allowing us to determine fairly accurately the physicochemical origins of the mechanical behavior of polymers [2,3].

Besides polymers, industry and nature provide us with a vast range of materials composed of complex polymeric elements in suspension in a liquid: emulsions, foams, and suspensions of solid particles. When the concentration of suspended elements is weak, the behavior of such materials is qualitatively similar to that of the interstitial liquid, which is generally Newtonian. At sufficiently high concentrations, the suspended elements develop specific mutual interactions and hence we usually deal with a "pasty" material, incapable of flow when the force exerted onto it is below a critical value. We currently encounter this type of material in our daily lives in products such as shaving foam, Chantilly, solar cream, cosmetic cream, mayonnaise, puree, paint, modeling paste, peanut butter, marmalade, and hair gel, or in natural phenomena such as mining slurries, mudflows, debris flows, lavas, snow, and lahars (water–ash mixtures on volcanic hill slopes). Civil engineering, food, and cosmetic industries also use pasty or granular materials for transporting or storing solid matter or for product forming, with agents such as drilling fluids, cement paste, concrete, mortar glues, ceramic slip, foodstuff pastes, sewage sludges, sand, grains, and powders.

In contrast to polymers, all these materials have extremely different internal structures, ranging from the packing of submicrometric, platelet, clay particles for muds, to the crowding of soft bubbles (with diameters in the high micrometer range) for foams. More critical is the fact that most industrial materials contain a wide range of elements of various sizes and interaction patterns (polymers in liquid suspensions or adsorbed by solid particles, colloidal particles interacting at a distance via electrostatic forces, formation of viscoelastic droplets or bubbles, grains interacting via friction or collision through the liquid, etc.). In this context one often focuses on a specific material and notes that it exhibits unique characteristics, which certainly is true from a physicochemical perspective. Such individual approaches unfortunately do not promote the development of a unifying approach to define the relationship between internal structure and mechanical properties for this wide class of materials. A new concept has emerged in physics, known as "jamming" [4], in which all these materials are perceived as "jammed" systems. Although this concept is not yet precisely defined, it concerns the "pasty" materials as defined above since this internal jamming implies that these materials cannot flow unless some outside force is applied to "unjam" this structure. In this field physicists essentially seek generic thermodynamic properties at the origin of the link between this jamming and the evolutions of the internal structure of these materials.

As I was studying various materials, I increasingly concluded that, considering the variety of internal structures of jammed materials, generic laws, if they exist, should be sought in the mechanical behavior of these materials. Indeed, in mechanics the specificities of the internal structure of each material may be put aside in favor of the qualitative characteristics of this internal structure, which induces different mechanical trends. The primary objective of this book is to propose a synthetic and general approach to define the mechanical behavior of pastes and granular materials.

In practice, it is critical to apply reliable rheometrical techniques for relevant characterization of materials, specifically, to measure some physical parameters related to the effective rheological behavior of the material. For pasty and granular materials this approach still constitutes a challenge for several reasons; for instance, these materials may exhibit a strongly nonlinear behavior [they behave either as solids or liquids depending on flow conditions], several experimental problems may occur (wall slip, fracture, drying, etc.) with these materials, and for some of these substances (granular materials) there may exist no constitutive equation intrinsic to the material (i.e., independent of boundary conditions). Finally, probably because of these difficulties, a variety of practical techniques for characterization of these materials in a rapid and robust way (slump test, Marsh cone, penetrometric measurement, etc.) involve "nonviscometric flows," specifically, flows that are more complex and controlled than the so-called viscometric flows used in rheometry. Often, each industrial field developed its own techniques that in fact involved the same basic flow types found in other fields. In this context the second major objective of this book was to review the experimental problems encountered with such materials and to examine the techniques used in different fields through the basic nonviscometric flows they involved, in order to propose theoretical analysis that would enable one to extract relevant rheological parameters from such tests.

This book is merely a sketch of what might be written on the topic of rheology. In the near future the development of new techniques for internal exploration of materials will probably give us a deeper insight into the behavior of pastes or granular materials, which will make rheometrical analysis even more accurate. However, the tools described here may provide an at least initially comprehensive approach to this field.

This work results from the research I have carried out since 1989. At first my motivation for the study of pasty materials was to provide protection against mudflows in mountain streams, initiated by M. Meunier in Cemagref and supervised by J. M. Piau in the Laboratory of Rheology in Grenoble. I undoubtedly enjoyed a perfect launching site and hopefully I was worthy of it since these individuals provided me with much of my scientific formation in different ways. Another key stage was my meeting with O. Coussy, the then head of LMSGC. Not content with teaching me the details of research management, he also boosted rheology research by creating a mainline around rheophysics in our laboratory.

During these years I had the opportunity to work with researchers whose ideas are reflected at various points in this book: C. Ancey (EPFL, Lausanne), who, among other things, introduced me to the specificities of granular materials; D. Bonn (LPS, ENS Paris), with whom we developed the very important concept of viscosity bifurcation; J. C. Baudez (Cemagref), who had a remarkable approach to the reconstruction of a velocity profile; and X. Chateau (LMSGC), with whom I am still daily discovering the subtleties of mechanics. Several individuals also kindly agreed to review parts of this book, expressed comments, and provided enlightening advice; I thank them warmly here, and hope that this work will be of some personal benefit to them as well: N. Alderman (Aspen Technology), G. Ovarlez (LMSGC), X. Chateau (LMSGC), B. Herzhaft (IFP), F. Chevoir (LMSGC), and S. Rodts (LMSGC). I would also like to thank John Wiley & Sons, Inc. for trusting me. Eventually, last but not least, many thanks to my wife, who managed once again to put up with seeing me somewhat tense, focused on a new objective for about 2 years.

REFERENCES

1. E. C. Bingham, *Fluidity and Plasticity*, McGraw-Hill, New York, 1922.
2. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1970.
3. P.-G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell Univ. Press, Ithaca, NY, 1979.
4. A. J. Liu and S. R. Nagel, *Jamming and Rheology*, Taylor & Francis, New York, 2001.

NOTATION

Roman Symbols

$\mathbf{a}$	acceleration vector
b	separation distance between the centers of two elements; half-height of a cylinder of material
$\mathbf{b}$	volume force
Ba	Bagnold number (see Section 2.3)
$\mathbf{B}$	magnetic field; buoyancy force
d	strain rate in elongational flow; characteristic element length (equivalent average diameter)
ds	surface element
dv	volume element
D	fluid width
D_{I}, D_{II}, D_{III}	invariants of the strain rate tensor
$\mathbf{D}$	strain rate tensor
E	elastic modulus of a solid particle
f	friction coefficient between two solid surfaces
F_c	critical force for incipient motion or stoppage
F_0	imposed force in squeeze flow
Fr	Froude number [equation (5.57)]
$\mathbf{F}_D$	drag force
$\mathbf{F}_t$	relative configuration gradient [equation (1.2)]
$\mathbf{g}$	gravity
G	elastic modulus for Maxwell model
G', G''	elastic and viscous moduli
$\mathbf{G}$	magnetic field gradient

h	thickness of fluid layer; separation distance between two solid surfaces
h_c	critical fluid thickness for incipient motion or stoppage
h_{stop}	critical granular material thickness at stoppage
h_0	uniform flow thickness for a granular material
H	gap between plates or disks; dimensionless fluid thickness; height
$H_{\vartheta<t}$	functional of a variable history (up to t)
i	slope angle of an inclined plane
i_c	critical slope for incipient motion or stoppage
$\mathbf{I}$	identity tensor
J_e	rate of evaporation
$k = \tan\varphi$	coefficient of friction of a granular material; permeability of a porous material; drag coefficient
k_c	critical drag coefficient
L	flow or object length
Le	Leighton number [equation (2.27)]
$\mathbf{L}$	velocity gradient tensor
M	torque
$\mathbf{M}$	magnetic moment (spin)
n	vapor density
$\mathbf{n}$	normal vector
N	normal force
p	pressure
p_f	pressure within the interstitial fluid of a granular paste
p_0	ambient gas pressure
P	energy stored or dissipated by mechanical action
q	flow rate by unit surface
$\mathbf{q}$	heat density flux
Q	flow rate (fluid discharge)
$\mathbf{Q}$	rotation (orthogonal) tensor
r_c	critical radius
r_0	radius of a capillary
r_1, r_2	inner and outer cylinder radii of coaxial cylinders
R	radius of a cylindrical object or material; dimensionless radial distance
Re	Reynolds number [equation (3.80)]
S	surface
St	Stokes number [equation (2.26)]
t	time
$\mathbf{t}$	stress vector
T	tangential force; temperature
$\mathbf{T}$	deviatoric stress tensor [equation (1.34)]
u	velocity in a simple shear between parallel plates
U	mean fluid velocity; maximum fluid velocity
U_s	slip velocity

v_x, v_y, v_z	velocity components in a Cartesian frame
v_r, v_θ, v_z	velocity components in a cylindrical frame
v_φ, v_θ, v_z	velocity components in a spherical frame
$\mathbf{v}$	velocity vector
V	dimensionless velocity; velocity of a solid object through a fluid; volume
W	work
$\mathbf{x}$	position at time t
$\mathbf{x}^*$	position in another frame of observation
y_c	critical height separating sheared and unsheared regions
x, y, z	coordinates in a Cartesian frame
r, θ, z	coordinates in a cylindrical frame
φ, θ, z	coordinates in a spherical frame
∇	gradient operator

Greek Symbols

η	apparent viscosity of a material
ς	shear stress function
β	yielding criterion coefficient
γ	simple shear deformation (or strain); gyromagnetic ratio
γ_c	critical deformation
γ_0	strain amplitude
γ_{LG}	interfacial tension between a gas and a liquid
$\dot{\gamma}$	shear rate
$\dot{\gamma}_{\text{app}}$	apparent (macroscopic) shear rate
$\dot{\gamma}_c$	critical shear rate
$\dot{\gamma}_{\text{eff}}$	effective (local) shear rate
$\dot{\gamma}_R$	shear rate at the periphery of a cylindrical sample
δ	slip layer thickness
Δp	pressure difference in a capillary flow
ϕ	volume fraction
ϕ_m	maximum packing fraction
φ	angle of friction of a granular material; phase shift
Φ	potential energy of interaction
λ	structure parameter
λ_m	maximum growth rate of instability
μ	viscosity of a Newtonian fluid; generalized coefficient of friction for granular flows
μ_0	viscosity of a Newtonian interstitial fluid
ω	rotation velocity of a fluid element; oscillation frequency; Larmor frequency
Ω	rotation velocity of a cylinder, a cone or a disk; fluid volume; particle volume
ρ	fluid density

ρ_p	solid particle density
ρ_0	interstitial fluid density
σ	normal stress
σ_{xx}, σ_{xy}, σ_{xz}, (etc.)	components of stress tensor
Σ_{I}, Σ_{II}, Σ_{III}	invariants of stress tensor
$\boldsymbol{\Sigma}$	stress tensor
$\boldsymbol{\Sigma}_f$	stress tensor component of interstitial fluid
$\boldsymbol{\Sigma}_g$	stress tensor component of granular phase
$\boldsymbol{\Sigma}_0$	stress tensor at initial time
τ	shear stress [equation (1.43)]
τ_c	critical or yield stress
τ_p	shear stress at wall
τ_0	shear stress amplitude
ϑ	time
χ	shear rate function
ξ	position vector at time ϑ

INTRODUCTION

The objective of this book is to provide useful tools for characterizing environmental or industrial pastes, slurries, and granular materials from a mechanical perspective. In particular, we aim at going beyond the basic rheometrical techniques with the help of sophisticated analysis of the rheological behavior of pastes and experimental artefacts and beyond the various existing qualitative approaches or comparative techniques by providing, as far as possible, relevant rheological interpretation of these practical tests.

Any rheological approach relies on a description of the motion within the frame[1] of continuum mechanics, and on the assumption of some mechanical behavior intrinsic to the material under study. In practice, very simple flows, specifically, viscometric flows, must be used because they provide straightforward relations between stress components and flow history. Although the validity of the underlying assumptions for such an approach (continuum medium, simple fluid) is clear for simple liquids, such as water, alcohol, and oil, it is not obvious for more complex materials such as pastes or granular materials. In Chapter 1 we review the tools used in continuum mechanics and the principles for expressing the constitutive equation of any material for the more general case. This, in particular, places pastes, slurries, and granular materials in an intermediate class, which may be referred to as "jammed systems," between solids and fluids. The

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[1] The term "frame" is used throughout the text to denote *frame of reference*, *perspective*, *framework*, *context*, or similar.

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peculiarity of jammed systems is that their constitutive equations can be of either the solid or fluid type depending on flow history. The usual viscometric flows and the corresponding methods of analysis are also reviewed taking into account as far as possible the specific behavior patterns of these materials.

Before studying the rheometrical techniques appropriate for jammed systems, it is necessary to have a clear idea about the rheological trends that must be accounted for. In Chapter 2 we propose a classification of the materials as a function of the qualitative rheological trends that they exhibit. We start by reviewing the main interactions between the different possible elementary components of these systems, and show how they qualitatively affect the rheological behavior of the materials. Finally, three main classes emerge:

1. *Pastes* (soft jammed systems), in which mainly soft interactions predominate and that are basically thixotropic, yield stress fluids
2. *Granular materials*, in which direct (hard) interactions between grains predominate, and whose "frictional regime" behavior is somewhat analogous with the behavior of two solids in contact and in relative motion
3. *Granular pastes*, in which either soft or direct interactions may predominate depending on the flow regime, and which thus can exhibit either a pasty or granular behavior depending on flow conditions

Setting up the constitutive equation of granular pastes (class 3 above) is still a tricky task. In this book the main developments concern classes 1 and 2 (i.e., pastes and granular materials), for which a significant set of knowledge appears to be available, bearing in mind that the behavior of granular pastes can be extrapolated from the behavior of the two extreme cases described above (classes 1 and 2), once their flow regimes have been determined. Moreover, only pasty materials exhibit an intrinsic behavior, independent of boundary conditions. Consequently, in Chapters 3–5 we focus on different aspects of paste rheometry. The granular materials in a frictional regime are considered in Chapter 6. Practical rheometrical tests for both material types are reviewed in Chapter 7.

Rheometry with pastes appears to be a difficult task because of their complex rheological behavior, which may include elasticity, solid–liquid transition, and thixotropy. Chapter 3 focuses on the rheometrical procedures for best-guess determination of these properties, and on the various measurement problems that may occur, such as wall slip, shear localization, surface tension, drying, phase separation, crack, temperature effects, and inertia effects, and may preclude a relevant interpretation of the data in terms of the effective, macroscopic behavior of the homogeneous material.

Soft jammed systems (and also granular materials) exhibit strong nonlinear rheological trends that may lead to severe heterogeneities or time variations of the flow field in viscometric flows. In general these phenomena cannot be properly appreciated from usual macroscopic measurements. A more sophisticated rheometrical approach, which we refer to as "local rheometry," consists in measuring and interpreting the flow field within the rheometer. In Chapter 4 we review the principles of the most versatile technique that may be used for this purpose: magnetic resonance imaging (MRI) velocimetry. Methods for interpreting measured velocity profiles within Couette geometry in terms of the constitutive equation of the material are then discussed. Finally, an alternative technique, "velocity profile reconstruction from rheometry," which enables us to directly view the velocity profiles over short timescales from the usual rheometrical tests, is presented.

In practice, it is seldom easy to carry out rheometrical tests under ideal conditions as required by theoretical viscometry because a sample must be taken from the fabrication process and placed in a laboratory rheometer of appropriate size (for the continuum assumption to be valid). This has led to the development of various practical techniques often involving flows that are nonviscometric [i.e., not characterized by relative motion (gliding) of parallel or concentric fluid layers over one another] but that nevertheless have some sufficiently simple properties for the extrapolation of paste rheological behavior under specific conditions. This is the case for the displacement of an object relative to the fluid, for the "squeeze" flow, or for the coating or spreading flows. In Chapter 5 we review the characteristics of these flows in the case of pastes and focus on how their macroscopic characteristics may be related to yield stress.

The rheology of granular materials cannot be determined from the usual rheometrical techniques, since they do not exhibit an intrinsic constitutive equation, independent of boundary conditions; hence granular flows can be described only under certain flow conditions. In Chapter 6, we review the characteristics of granular flows for which a frictional regime may take place: viscometric flows, free surface flows, conduit flows, compression flows, and free surface flows for granular pastes. In most cases, simple relationships describing flow characteristics in terms of the friction coefficient can be established. These flows can then be used as rheometrical tests for granular materials.

Many practical tests have been developed in different industries for characterizing the rheological behavior of pastes or granular materials. Most of them provide one single parameter that may be used for comparison between materials but does not find a clear rheological interpretation. In Chapter 7 we review the main different practical tests and show that for most of these tests it is possible to find a relevant rheological interpretation of the measured parameter if an appropriate experimental procedure is respected. Afterward we review the main types of industrial and environmental materials, discuss their classification (within the three main categories of materials: pastes, granular pastes, or granular materials), and suggest the most appropriate practical rheometrical test to be used with each type.

CHAPTER 1

MATERIAL MECHANICS

1.1 INTRODUCTION

Any rheological approach relies on a description of the motion within the frame of continuum mechanics, and on the assumption of some mechanical behavior intrinsic to the material under study. In practice, in order to determine this behavior, one uses viscometric flows that, because of their simplicity, provide straightforward relations between stress components and flow history under certain conditions. The theory of viscometric flows, which provides a complete theoretical frame for analyzing such data in rheological terms, has nevertheless been developed within the frame of a specific class of materials, *simple fluids*, which have a vanishing memory.

Although the validity of these assumptions (continuum medium, simple fluid) is clear for simple liquids, such as water, alcohol, and oil, it is not obvious for more complex materials such as pastes or granular materials. Indeed, we often observe these materials to be strongly heterogeneous at our scale of observation, and thus may question the validity of the continuum assumption. Moreover these materials may have a dual behavior, behaving like solids under some conditions and liquids under other conditions. For example, powders or foams remain stationary like a solid under the action of gravity alone, but begin to flow like a liquid under vibration (powders) or squeezing (foams). Various pasty materials also exhibit time-dependent properties; their viscosity may continuously increase when left at rest but, during flow, may decrease in time. Thus, pastes and granular materials cannot be considered a priori as simple fluids with vanishing memory.

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There is thus a need to review the basic tools of (continuum) fluid mechanics and rheometry in a more general frame including the specificities of pastes and granular materials. In this context we first review the definitions and principles of continuum mechanics and their physical origin, focusing on the validity of the continuum assumption for pastes and granular materials (Section 1.2). Then we examine the role and structure of the constitutive equation, and show that pastes and granular materials belong to a class intermediate between solids and fluids (Section 1.3). Usual viscometric flows and the corresponding methods of analysis are reviewed in Section 1.4 taking into account as far as possible the specific behavior pattern of these materials.

1.2 CONTINUUM MECHANICS

1.2.1 Definition of a Material

A *material* can be defined as the ensemble of elements of matter contained in a connex volume. The fact that we identify this ensemble as a single material means that in any two parts of this volume we would find similar ensembles of elements of matter. Nevertheless, for any given material, this definition would probably fail if viewed on the scale of some basic components of this matter (atoms, molecules, bubbles, solid particles, etc.), since on this scale the material clearly varies from one (very small) part to another. This implies that our evaluation of the material in a given part must account for a certain number of basic components over which we can proceed to some average of a physical property q (see Figure 1.1). It follows that the minimum scale (l) on which one can reasonably "observe" the system and effectively consider it as a material

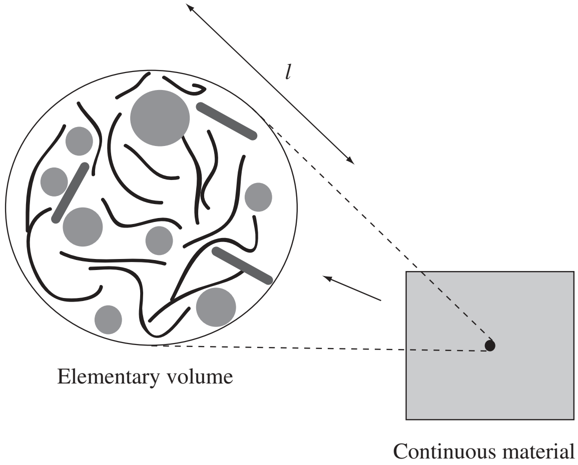

Figure 1.1 Aspect of an elementary volume (left) of a material, continuous on our scale of observation (right), but including different types of matter.

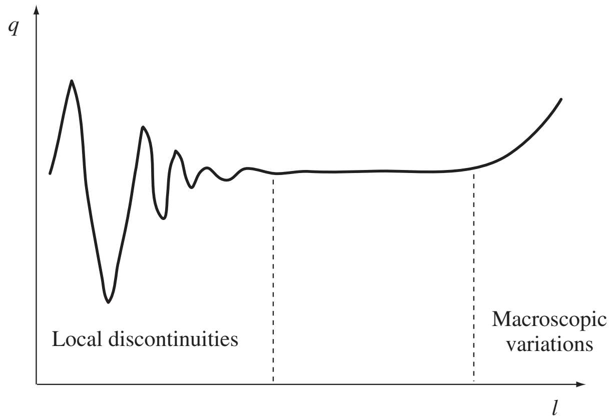

Figure 1.2 Variation of a physical property (q) averaged over a given volume of material as a function of the extent of this volume (l).

(i.e., the minimum volume of a given part of the system) corresponds to the point beyond which the result of this (q) average no longer varies when this scale further increases (see Figure 1.2). These volumes will be referred to as *elementary parts* (or *volumes*) of the material, while the basic components identified above will be referred to as the *elements*. However, it is worth noting that, when further increasing the scale of observation, macroscopic variations resulting from thermal and/or mechanical constraints imposed to the material begin to play a role (see Figure 1.2). These variations are precisely the phenomena that continuum mechanics or thermodynamics intends to describe with the help of mathematical concepts. The appropriate scale of elementary parts is thus situated between the range of rapid variations of q due to matter discontinuity and the range of macroscopic variations. When these two ranges recover, it is not possible to consider the system under the continuum assumption, as the flow is in a "discrete" regime.

1.2.2 Continuum Assumption

The material can thus be considered as *continuous* when the averages of physical properties (density, force, velocity, temperature, etc.) over the elementary parts of the material slowly vary from one such part to one of its neighboring parts. More precisely, the continuum assumption implies that the physical variables, which assume the values of property averages, may be described by continuous and continuously derivable functions of space and time. This will make it possible to describe the material evolutions from a set of equations relating an ensemble of variables and their changes in time and space. Such an approach opens the

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