I Introduction

I.1 Basic concepts

The understanding of nature is one of the most important ends of studying physics. Throughout this way there are some questions that have been concerning scientists for many centuries. After all, of which things is the universe constituted? How can matter be found in nature? What is the behavior of different materials under stress? How is it possible to classify different materials? In order to clear up the physics that this thesis deals with, a review of some basic concepts is realized in this section.

A good start is by the definition of a chemical substance, since in most of the everyday experience it is common to deal with a lot of them. So, a chemical substance can be defined as a portion of matter with a specific chemical composition, i.e. constituted by only one chemical compound [1]. The physical state of a sample of a substance is defined by its physical properties, therefore two samples of a substance that have the same physical properties are in the same physical state [2].

In fact, not all matter in the universe is found as chemical substances, so that in a classical approach it is possible to state that all matter exists in nature in one of four physical states: solid, liquid, gaseous, or plasma.

Any matter in the plasma state possess distinct physical properties than in all of three others states, and therefore plasma is usually considered the fourth physical state of matter. A plasma has neither a definite shape nor definite volume as gases, but a matter in the plasma state has a strong response to electromagnetic fields, for example, since a plasma is constituted by free ions and electrons [3]. In spite of being the most common state of matter in the universe (stars are constituted by matter in the plasma state), in the present work only the three others lower-energy physical states of matter (solid, liquid, and gaseous) will be discussed.

A portion of matter in the solid state (a solid body) has both definite shape and definite volume at a given temperature and pressure. In this physical state, the atoms, molecules, or ions composing the body are very close to each other, arranged in a definite organized geometric configuration, characteristic of the chemical compounds constituents [4]. This crystalline microstructure, observed by sharp Bragg reflections in a diffraction experiment, leads a solid body to possess some specific macroscopic physical properties [5]. One of them is the mechanical response of a material in the solid state to a shear stress applied. When a defined shear stress is applied to a solid body, a corresponding deformation is begotten, provided that the elastic limit of the material was not exceeded. Once the shear stress is moved away from the body, the initial shape is recovered. This behavior is described by Hooke's law, which state that the shear stress applied to a solid body is proportional to the deformation begotten, and the proportional factor is the elastic modulus, which depends on the temperature. A useful interpretation of this equation is that a solid body, due to its close organized crystalline microstructure, "remembers" its initial shape, and hence this elastic behavior is associated to the material "memory" [6]. Another macroscopic behavior of matter in the solid state is the fact that a solid body can be anisotropic, i.e. their mechanical properties can depend on the orientation of deformation with respect to the crystallographic axes [7]. The physical properties of an anisotropic solid body are different depending on the direction considered, which is a very important characteristic to be taken into account in some engineering applications.

On the other hand, a portion of matter in the gaseous physical state can neither has a definite shape nor a definite volume. A gas always fills completely any container that it occupies, adopting its shape. Moreover, different from the solid state, in the gaseous physical state the atoms or molecules that compound a gas are widely separated and in continuous random motion (the Brownian motion) [2, 4]. Due to the large distance among atoms or molecules in a gas, the effects of the intermolecular forces are considerably weak when compared to the ones in the solid state, making the Brownian motion possible. Furthermore, the velocity of this motion increases when the temperature of the gas is raised, which causes more collisions between atoms or molecules [2]. Another difference from a solid body is that a gas is always isotropic, i.e. its physical properties are the same in all directions. Moreover, when a shear stress is applied to a gas, no matter its magnitude, this portion of matter in the gaseous state (which received the shear stress applied) starts to deform continuously. When the shear stress is removed, the gas experienced a plastic deformation, and hence it cannot "remember" its initial position. This behavior is described by Newton's law of viscosity which state that the shear stress applied to a portion of matter in the gaseous state (or sometimes in the liquid state) is proportional to the shear rate begotten, and the proportional factor is the viscosity, which depends on the temperature and pressure.

The liquid state of matter is much more complex than either the solid or gaseous states [8]. In the liquid physical state, a portion of matter has intermediate properties between the solid and gaseous states. As a solid, a liquid has a definite volume at a given temperature and pressure. However, as a gas, a liquid has no definite shape, adopting the shape of the container in which it is placed [4]. Moreover, in the liquid state, the atoms, molecules, or ions are neither in a close organized geometric configuration (crystalline microstructure) as in the solid state, nor widely separated as in the gaseous state. Hence, in the liquid state the intermolecular forces play a much greater role than in the gaseous state [9]. Thus, a satisfactory model of the liquid state can neither consider the molecules independent, nor as having a constant number of nearest neighbors, as in a crystalline microstructure [10]. Therefore, in the liquid state, the atoms, molecules, or ions are relatively close when compared to the gaseous state, but the regular structure characteristic of the solid state is only observed in small regions, since liquids give no sharp Bragg reflections, but diffuse rings in diffraction experiments [5]. Furthermore, as the molecules are close to each other and in continuous motion, it is possible that confined liquids transmit equally in all directions the pressure applied to them [11]. In relation to its mechanical properties, a portion of matter in the liquid state is always isotropic, as gases [7]. Moreover, as in the gaseous state, in the liquid state a portion of matter deforms continuously under the application of a shear stress, no matter its magnitude.

Due to the similarity between liquids and gases, with respect to the mechanical behavior under shear, the term fluid is usually employed so as to refer to liquids and gases. The definition of a fluid can be found in an introductory book of fluid mechanics [12, 13, 14]. A common definition is that "a fluid is a substance, or a mixture of substances that deforms continuously under the application of a shear stress, no matter how small the shear stress may be."

A simple pure substance, as pure water for example, can be found in nature in one of three lower-energy states of matter, depending on the temperature and pressure. In fact, under certain conditions of temperature and pressure (critical or triple point), a simple pure substance may exist and be stable in all three physical states (solid, liquid, and gaseous) at the same time [4, 9].

One other important basic concept is the idea of phase. A phase is a form of matter that is uniform throughout not only in chemical composition, but also in physical state [2, 15]. By this definition, pure water in its critical point, for example, exist in three phases in equilibrium, a solid, a liquid, and a gaseous phase. Other phase distinction is made when two or more allotropes of the same substance, and in the same physical state of matter exist in a system as the white and black allotropes of phosphorus, or the graphite and diamond. It is also possible that a mixture of different substances originate a two, or a multi-phase system in which only one physical state of matter is present, as in a mixture of oil in water (a two-phase system). Finally, the most obvious distinction of different phases is when a substance in one physical state is mixed in another substance in a different physical state — it happens in suspensions, for example sand mixed in water.

The classical approach, which defines four physical states of matter (solid, liquid, gaseous, and plasma), cannot fully classify all matter found in the universe but is a useful tool for understanding material physics. In fact, everyday it is common to deal with materials which have an intermediate physical properties among the lower-energy classical states of matter, such as glasses, amorphous solids, suspensions, colloids, emulsions, and foams. These materials can be considered complex materials since their physical properties are not exactly the same as classical solids, liquids and gases. Other examples of complex materials are polymeric liquids and melts, liquid crystals and micellar solutions [7].

Glasses and amorphous solids for example are useful materials for technological applications. They are rigid, non-crystalline materials, usually obtained by supercooling of a liquid [16]. When a liquid is cooled beyond its equilibrium freezing point, there are two possible events that can occur. First, the liquid can crystallize, changing to the solid state. Second, if the cooling rate is fast enough that nucleation to the crystal does not occur, then the supercooled liquid will undergo a transition to a glass [17]. Amorphous solids can be prepared by other unusual methods such as dehydration process. These materials, prepared by other methods, can exhibit a glass transition or not [16], and it is the existence of this transition that differentiates a glass from other amorphous solids. The glass transition is characterized by a dramatic increase in the viscosity and a sharp, but not discontinuous, change in slope of the extensive thermodynamic variables, such as entropy and molar volume [17]. Despite that particularities both glasses and amorphous solids yield quite similar X-ray diffraction patterns to those of dense liquids. In addition, these materials are isotropic [9], and flow very slowly under a shear stress applied, no matter how small the shear stress may be. Hence, both materials can be viewed as very high viscosity liquids with their disorder frozen in [9], despite looking as solids.

On the other hand, suspensions, colloids, emulsions, and foams are dispersions of microstructures in a homogeneous phase and can be found in many industries. All these materials usually presents a yield stress, i.e. a critical stress below which no plastic deformation is observed, and above which the material flow (classical definition). Therefore, according to the classical definition, below the yield stress no flow is observed in these materials, so that they behave as solids. However, when a shear stress higher than the yield stress is applied to one of these materials, they flow as liquids.

Complex materials as those examples above are constituted by molecules or microstructures with length scales much larger than atomic [7]. These materials are frequently composed by a mixture of substances in one or more phases, involving one or more states of matter. Due to its complex structure, in this kind of materials, there are a lot of micro-scale interactions which cannot be found in simple substances. This interactions lead complex materials to possess mechanical properties that are intermediate between classical solids and liquids [7]. Specification of a viscosity or an elastic modulus does not even begin to describe the mechanical properties of such a material. The number of recognizably different kinds of complex materials has gradually increased throughout last century, so that it is now possible to find materials that possess to an intermediate degree almost of any of the properties that distinguish classical solids from liquids [7]. So, the classical approach which distinguishes solids, liquids and gases are not always clear enough to classify the complex materials. Thus, in this work the term material will be employed everywhere to refer a substances or a mixture of substances that can behave from classical liquids or solids to a complex material. Moreover, the terms solid, liquid or gas will be used to refer a substances that can be classified in the classical approach of the states of matter described above.

I.2 Viscoplastic materials

The classical concept of materials which can be classified as a viscoplastic one, due to its rheological behavior, means that below a threshold stress, called yield stress, a viscoplastic material has a solid-like behavior, i.e. it does not flow. However, beyond the yield stress, the viscoplastic material has a liquidlike behavior and flow, with a dramatically drop in its viscosity.

Contradicting the classical concept of a viscoplastic (or yield stress) material, Barnes and Walters [18] argued, by showing some data, that the yield stress concept is an idealization, and that, given accurate rheological measurements, no real yield stress exist.

Four years later, Hartnett and Hu [19] performed an experiment using the falling ball technique and a Carbopol dispersion as a viscoplastic model material to demonstrate that for practical purposes the yield stress exist. In their words "the yield stress is an engineering reality".

One year later (1990) Astarita [20] published a letter discussing about the disagreement between Barnes and Walters, on one side, and Hartnett and Hu on the other side. After all, is the yield stress a myth or an engineering reality? For Astarita [20], the question is formulated the wrong way. In his opinion "the answer depends on what the problem is".

Nine years later, Barnes [21, 22] performed a comprehensive review about yield stress materials, reviving the argument that the property "yield stress" actually does not exist. The results of a number of examples measurements in real materials usually classified as viscoplastic are presented in these papers, where flow is observed even when the stress level falls below what he calls an "apparent yield stress".

In 2007, Piau [23] published a paper in which a falling ball experiment in Carbopol dispersion, similar to the one realized by Hartnett and Hu was performed. After ten months he concluded that "hardly any creep was observed".

In those articles by Barnes [21, 22], and also in most of the literature on viscoplastic materials, the term "yield stress" implies a stress below which no plastic deformation is observed (the classical concept). This is consistent with the pioneer Bingham viscosity function for viscoplastic materials, explaining perhaps the adoption of this definition by the scientific community. Therefore, the usual understanding of yield stress implies that no plastic deformation whatsoever is admitted at a stress that falls below it, i.e. a threshold stress can only be legitimately called yield stress if two requirements are met, namely, (i) some microstructure collapse occurs when the threshold stress is exceeded, causing a dramatic viscosity drop, and (ii) there is complete absence of plastic deformation at stresses below it.

It is worth emphasizing that the classical concept of yield stress is bound to the steady-state flow curve of a given material, and therefore any thixotropic or elastic behavior observed before the achievement of the steady state is totally irrelevant to it. This seemingly evident fact is nevertheless often overlooked, which is a source of a great deal of confusion in the related literature.

Barnes [21, 22], in his articles, used the term "liquid" to refer to a viscoplastic material, once if the yield stress does not exist, a viscoplastic material would deform continuously under the application of a shear stress, no matter its magnitude, as a classical liquid. However, materials which has

a viscoplastic behavior are usually composed by a mixture of substances in different states of matter (as suspensions, and foams). Furthermore, due to the complex structure of a viscoplastic material, there are some micro-scale interactions that does not exist in a classical liquid. In addition, the existence or not of a real yield stress still remains under discussion, therefore in the present work, materials which has a viscoplastic behavior will be called "viscoplastic materials" in spite of "viscoplastic liquids", which seems to be an inappropriate term.

I.3 Viscoplastic materials models

Viscoplastic materials were first modeled by the Bingham viscosity function as follows:

$$\eta = \begin{cases} \infty, & \text{if } \tau \leqslant \tau_0; \\ \frac{\tau_0}{\dot{\gamma}} + \mu_0, & \text{if } \tau > \tau_0. \end{cases}$$
(1)

where μ_0 is the plastic viscosity, and τ_0 is the yield stress.

One other common model is the Herschel-Bulkley equation, sometimes known as the generalized Bingham.

$$\eta = \begin{cases} \infty, & \text{if } \tau \leqslant \tau_0; \\ \frac{\tau_0}{\dot{\gamma}} + K \dot{\gamma}^n, & \text{if } \tau > \tau_0. \end{cases}$$
(2)

where K is the consistency index, n is the power-law index, and τ_0 is the yield stress.

These are the most used models for representing the viscosity behavior of a viscoplastic material. Although, both the Bingham, Eq. (1), and Herschel-Bulkley equations, Eq. (2), carry a problem with respect to the infinity viscosity when the stress is below the yield stress. This infinity viscosity turns this equations unsuitable to numerical simulations of flows. This problem is usually circumvent by employing equations with a regularization parameter which change the infinity viscosity to a high constant value.

One of these regularized models was proposed by de Souza Mendes and Dutra [24]:

$$\eta = \left(1 - \exp\left[-\frac{\eta_o \dot{\gamma}}{\tau_o}\right]\right) \left(\frac{\tau_o}{\dot{\gamma}} + K \dot{\gamma}^{n-1}\right) \tag{3}$$

in this equation, $\dot{\gamma}$ is the shear rate, and the parameters η_o , τ_o , K, and n, are respectively the low shear rate viscosity, the yield stress, the consistency index, and the behavior or power-law index [24].

According to Eq. (3), when the stress τ reaches the yield stress τ_o , there is a sharp increase of the shear rate with no appreciable change in stress, i.e. the shear stress remains roughly equal to τ_o while the shear rate value jumps from a value around $\dot{\gamma}_o$ to an often much larger value in the vicinity of $\dot{\gamma}_1$, where

$$\dot{\gamma}_o \equiv \frac{\tau_o}{\eta_o}; \qquad \dot{\gamma}_1 \equiv \left(\frac{\tau_o}{K}\right)^{1/n}$$
(4)

The jump number J proposed by de Souza Mendes [25] gives a relative measure of the shear rate jump that occurs at $\tau = \tau_o$ [26]:

$$J \equiv \frac{\dot{\gamma}_1 - \dot{\gamma}_o}{\dot{\gamma}_o} = \frac{\eta_o \tau_o^{\frac{1-n}{n}}}{K^{1/n}} - 1 = \frac{\dot{\gamma}_1}{\dot{\gamma}_o} - 1 = \frac{1 - \dot{\gamma}_o^*}{\dot{\gamma}_o^*}$$
(5)

The jump number is thus a dimensionless rheological property of viscoplastic materials. When n = 1, it becomes independent of the yield stress τ_o and reduces to $J = \eta_o/K - 1$, i.e. for n = 1, J + 1 becomes the ratio between η_o and the plastic viscosity.

Choosing $\dot{\gamma}_1$ as characteristic shear rate and τ_o as the characteristic stress, so that $\tau^* \equiv \tau/\tau_o$ and $\dot{\gamma}^* \equiv \dot{\gamma}/\dot{\gamma}_1$ are respectively the dimensionless versions of the shear stress and shear rate, then it is possible to write the following dimensionless form of Eq. (3) in terms of stress [27]:

$$\tau^* = (1 - \exp\left[-(J+1)\dot{\gamma}^*\right])(1 + \dot{\gamma}^{*n}) \tag{6}$$

This function is shown for n = 0.5 in Fig. I.1, for the jump number range $100 < J < \infty$. As $J \to \infty$, the Herschel-Bulkley equation is recovered.

The dimensionless viscosity function is given by

$$\eta^* = \frac{\tau^*}{\dot{\gamma}^*} = \frac{\eta}{\eta_o} (J+1) = (1 - \exp\left[-(J+1)\dot{\gamma}^*\right]) \left(\frac{1}{\dot{\gamma}^*} + \dot{\gamma}^{*n-1}\right)$$
(7)

The scaling presented above involves material properties only, and thus the resulting dimensionless quantities are also material properties. However, it is only suitable for viscoplastic materials, because the characteristic quantities τ_o and $\dot{\gamma}_1$ are both null for Newtonian and power-law materials.



Figure I.1: The dimensionless shear stress function.

It is interesting to observe that the regularization parameters that appear in the regularized Bingham equations are closely related to the jump number. Indeed, if the same scaling applied to obtain Eq. (7) is also applied to the regularized Bingham equation proposed by Bercovier and Engelman [28], then this equation assumes the following form:

$$\eta^* = 1 + \frac{1}{\dot{\gamma}^* + 1/J} \tag{8}$$

Similarly, the viscosity function proposed by Papanastasiou [29] becomes

$$\eta^* = (1 - \exp\left[-J\dot{\gamma}^*\right])\frac{1}{\dot{\gamma}^*} + 1$$
(9)

while the bi-viscosity equation takes the following dimensionless form:

$$\eta^* = \begin{cases} \frac{1}{\dot{\gamma}^*} + 1, & \text{if } \dot{\gamma}^* > 1/J; \\ J+1, & \text{otherwise.} \end{cases}$$
(10)

Therefore, for all cases, the (dimensionless) regularization parameter – to which no physical meaning is attributed in the literature – is in fact the jump number J itself, a measurable rheological property of viscoplastic materials.

I.4 Overview

Complex materials which behave as a viscoplastic one are found in a lot of natural processes, and in a wide variety of industries such as food, cosmetic, farmaceutical and petroleum. In these industries, knowing the accurate rheological properties of a viscoplastic material and its behavior in different flows are fundamental for the success of many operations. Nevertheless, the measurements of the rheological properties of this kind of material still presents some challenges, such as yield stress measurements, apparent wall slip, thixotropy and the breakdown of structure on loading the material into the rheometer geometry used. In addition to that, until now some phenomena in different flows involving viscoplastic materials are not well understood, which require more investigation.

This thesis deals with viscoplastic materials, their rheological properties measurements, and their behavior in different kinds of flow. In chapter II an analysis of some viscometric flows and its inherent phenomena, involving viscoplastic materials is performed. The results found in chapter II was previous presented in the III Brazilian Conference on Rheology, in the Workshop on Viscoplastic Materials in Monte Verita – Switzerland, and recently in the 12^{th} Brazilian Congress of Thermal Engineering and Sciences. In chapter III the expansions-contractions flows involving viscoplastic materials are investigated, both by experiments and by numerical solution of the governing equations. These results were published in 2007 in the Journal of Non-Newtonian Fluid Mechanics vol. 142, pages 207-217. Chapter IV deals with the displacement of a viscoplastic material by air in capillary tubes. The results showed in chapter IV were also published in 2007 in the Journal of Non-Newtonian Fluid Mechanics vol. 145, pages 30-40. Finally, in chapter V the displacements of viscoplastic materials in oil wells are analyzed. Some results of chapter V were presented and published at the Offshore Mediterranean Conference and Exhibition 2007 in Ravenna — Italy, and some other results were recently presented in the IV Brazilian Conference on Rheology and in the International Conference on Rheology 2008.

I.5 Note

In this chapter it was realized an introduction to viscoplastic materials. In Sec. I.1 some basic concepts were defined so as to clear up the physics involved. Sec. I.2 deals with viscoplastic materials and its inherent phenomena. Sec. I.3 cover the models used to describe the viscoplastic rheological behavior. And finally, Sec. I.4 is an overview of the thesis. Secs. I.1, and I.2 was written based on a bibliography review realized by myself, and Sec. I.3 is based on previous works in which I collaborated led by prof. de Souza Mendes.