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Microfluidic rheometry

Christopher J. Pipe [a,*], Gareth H. McKinley [b,*]

[a] State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Hatsopoulos Microfluids Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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ABSTRACT

The development and growth of microfluidics has stimulated interest in the behaviour of complex liquids in micro-scale geometries and provided a rich platform for rheometric investigations of non-Newtonian phenomena at small scales. Microfluidic techniques present the rheologist with new opportunities for material property measurement and this review discusses the use of microfluidic devices to measure bulk rheology in both shear and extensional flows. Capillary, stagnation and contraction flows are presented in this context and developments, limitations and future perspectives are examined.

1. Introduction

Over the past decade the study of flows in geometries with characteristic length-scales of less than 100 μm has flourished (Stone et al., 2004; Whitesides, 2006). Developments in techniques for investigating and manipulating such flow configurations have been driven by recent advances in microfabrication techniques allowing the cheap and reliable manufacture of geometries with micron-scale feature resolution (Quake and Scherer, 2000; Ng et al., 2002; Marrian and Tennant, 2003) combined with the trend of miniaturization in the biotechnology, manufacturing and chemical processing industries. Common microfluidic device applications include coating flows, formation of suspensions, emulsions and foams, heat transfer and flows in lab-on-a-chip devices (Obot, 2002; Hansen and Quake, 2003; Stone et al., 2004; Squires and Quake, 2005). Many of these ultimate applications involve handling fluids that have a complex microstructure and the flow of these materials may give rise to non-Newtonian phenomena (Bird et al., 1987; Larson, 1999). In order to optimize the design and implementation of microfluidic systems, a detailed understanding of the bulk flow of complex liquids on small scales is clearly desirable.

Classical macroscopic rheometry techniques for measuring fluid properties in shear and elongation typically involve characteristic length-scales $O(1\ \mathrm{mm})$, require sample volumes $O\ (1\ \mathrm{ml})$ and probe deformation rates of perhaps up to $O(100\text{–}1000\ \mathrm{s}^{-1})$ (Macosko, 1994; Petrie, 2006). While these methods are satisfactory for understanding the behaviour of many fluids in a wide variety of flows, there are circumstances when using devices with smaller length-scales to investigate rheological responses may be advantageous. These include exploring sensitivity to interfacial conditions, probing large deformation rates in the absence of inertia or viscous heating, measuring flow phenomena when device length-scales approach those of the underlying material microstructure and the possibility of studying sample volumes on the order of

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* Corresponding authors.
E-mail addresses: chris@lnm.imech.ac.cn (C.J. Pipe), gareth@mit.edu (G.H. McKinley).

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nanolitres. Straightforward adaptation of classical macro-scale devices to incorporate micrometric length-scales has been shown to be effective for measuring shear properties under certain conditions; however, it becomes necessary to incorporate large correction factors to compensate for flow non-idealities (Connelly and Greener, 1985; Duda et al., 1988; Pipe et al., 2008) or to develop advanced opto-mechanical subsystems to ensure precise alignment (Dhinojwala and Granick, 1997; Clasen and McKinley, 2004). Moving down to molecularly thin films of complex liquids, atomic force microscopy (MacKintosh and Schmidt, 1999) and surface force apparatus instruments (Mukhopadhyay and Granick, 2001) have been used to study nano-scale rheology (Meyer et al., 1998); however, once again severe instrument artifacts can overwhelm the observations (McKenna, 2006). Despite the strong impetus driving the miniaturization of rheometric instrumentation, the ability of macro-scale systems to probe the bulk rheology of a fluid at the micro-scale has remained limited, largely because shrinking down some mechanical subsystems such as torsional motors and torque transducers is impractical. The arrival of microfluidic technology, however, has opened significant new possibilities for exploring the behaviour of complex liquids in micron scale geometries: not only does it allow the precise, rapid and cheap development of small scale devices but it also provides the ability to integrate rheological devices with other microfluidic components for lab-on-a-chip devices, opening new lines of application.

We review some of these recent developments in the present article: among a range of techniques situated at the junction of microfluidics and rheology we focus on the use of microfluidic devices to measure bulk rheological properties in shear and extensional flow. A very brief summary of other key approaches is given below and the reader is directed to the references provided for further information regarding these methods:

- Particle-based methods can be used to estimate the local rheological response due to the motions of nano-scale particles (Waigh, 2005; Larson, 2007). Systems can be 'passively driven' where the motions of particles due to thermal fluctuations are analyzed (Weitz and Pine, 1992; Starrs and Bartlett, 2003) or 'actively driven' where forces exerted on beads are measured using optical traps (Meiners and Quake, 2000; Brau et al., 2007) or magnetic tweezers (Bausch et al., 1998).
- The dynamics of single polymers, especially fluorescently labeled DNA, freely undergoing shear or extensional flow can be directly observed under certain conditions (Perkins et al., 1997; Smith et al., 1999; Hur et al., 2001) and related to the macroscopic rheological response measured in conventional rheometers. The use of DNA solutions as a model polymer system for probing the dynamics of flexible chains in different flow types is reviewed comprehensively by Shaqfeh (2005).
- Microfluidic devices can also be used to control the creation of droplets in a repeatable manner (Thorsen et al., 2001; Anna et al., 2003; Link et al., 2004), allowing the dynamics of single or groups of droplets to be explored, an important step in understanding the rheology of multiphase liquids.
- Microfluidic studies of ordered complex fluids, such as liquid crystals, can be used to impose well-defined structural and orientational boundary conditions on length-scales comparable to the dimensions of the observed order (Choi et al., 2004; Shojaei-Zadeh and Anna, 2006).

This review is arranged in the following order: Section 2 evaluate microfluidic capillary techniques for measuring the steady shear viscosity; in Section 3 we discuss microfluidic stagnation point flows; and in Section 4 we examine microfluidic contraction flows for measuring extensional properties. Finally, we assess perspectives for future work on microfluidic devices for investigating the rheology of complex liquids.

1.1. Device and fluid length-scales

We take the working definition for a microfluidic system as a device with at least one characteristic length-scale d in the range $1 \leqslant d \leqslant 100$ μm. For complex liquids the continuum hypothesis is still considered to be valid at such length-scales, but this may not be the case for flows of gases when the ratio of the mean free path l_f to the smallest characteristic dimension is of order $l_f/d \sim 0.001$ and compressibility becomes important (Colin, 2005). The microstructural length-scales of complex liquids, such as the radius of gyration of a polymer chain or a characteristic radius of a suspended particle, typically vary from 1 nm to 10 μm, and as such the working fluid may not be well approximated as microstructurally homogeneous. Additionally, as the characteristic length-scale of the flow geometry approaches that of the fluid microstructure, physical confinement can alter the dynamical evolution of the microstructure (Chen et al., 2004; Stein et al., 2006) and must be taken into account when considering the bulk response.

1.2. Surface effects

The ratio of surface area S to volume V for a fluid element is proportional to $S/V \sim d^{-1}$ and therefore moving towards smaller characteristic length-scales increases the relative importance of surface interactions compared to the behaviour of the bulk. While the classical 'no-slip' hypothesis at a smooth solid–fluid interface is generally regarded valid down to length-scales of 10 nm (Lauga et al., 2007), interactions at surfaces may lead to substantial apparent slip. Thus depletion layers are a potential source of non-homogeneity in the sample being investigated (Barnes, 1995; Granick et al., 2003) and may affect the measured rheological response. Apparent slip can be caused by surface roughness, the confining effect of the walls causing solute-poor regions near the wall, hydrophilic/hydrophobic interactions at interfaces and the influence of electrical properties in ionic liquids or liquids containing charged particles (Lauga et al., 2007; Voronov et al., 2008).