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Brownian dynamics simulations of planar mixed flows of polymer solutions at finite concentrations

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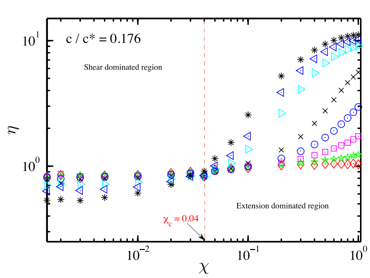
HIGHLIGHTS

- A multi-chain Brownian dynamics simulation algorithm has been developed.
- Periodic boundary conditions for planar mixed flows have been implemented.
- The effect of shear rate and extension rate on polymer size and viscosity is examined.
- A critical value of flow mixedness decides if flow is shear or extension dominated.

GRAPHICAL ABSTRACT



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ABSTRACT

Periodic boundary conditions for planar mixed flows are implemented in the context of a multi-chain Brownian dynamics simulation algorithm. The effect of shear rate $\dot{\gamma}$, and extension rate $\dot{\epsilon}$, on the size of polymer chains, $\langle R_e^2 \rangle$, and on the polymer contribution to viscosity, η, is examined for solutions of FENE dumbbells at finite concentrations, with excluded volume interactions between the beads taken into account. The influence of the mixedness parameter, χ, and flow strength, $\dot{\Gamma}$, on $\langle R_e^2 \rangle$ and η, is also examined, where $\chi \to 0$ corresponds to pure shear flow, and $\chi \to 1$ corresponds to pure extensional flow. It is shown that there exists a critical value, χ_c, such that the flow is shear dominated for $\chi < \chi_c$, and extension dominated for $\chi > \chi_c$.

1. Introduction

The study of the rheological behaviour of polymer solutions under different flow conditions has always been of great interest to the rheology community, both from a fundamental, and a practical point of view (Bird et al., 1987a; Larson, 1999). The most commonly studied flows are shear and elongational flows because of their simplicity. They have proven to be useful in understanding many industrial processes, such as extrusion, injection molding and sheet casting, to name but a few (Baird and Collias, 1998). In many practical situations, however, rather than only shear or elongational flow, a combination of these flows is often observed. A special case is the linear combination of shear and elongational flow, the so-called *mixed flow* (Fuller and Leal, 1981; Hur et al., 2002; Woo and Shaqfeh, 2003; Dua and Cherayil, 2003; Hoffman and Shaqfeh, 2007). While elongational flows are shear free flows, shear flows have equal contributions from vorticity and elongation. In mixed flows both elongational and rotational components exist but their contributions vary, characterized by a

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mixedness parameter χ. In the limit $\chi \to 0$, the flow reduces to shear flow, while the limits $\chi \to -1$ and $\chi \to 1$ correspond to pure rotational and pure elongational flow, respectively. Experimentally, mixed flows have been generated and studied using the four-roll mill (Lee et al., 2007). While there have been relatively few computational studies of mixed flows of dilute polymer solutions (Hur et al., 2002; Woo and Shaqfeh, 2003; Dua and Cherayil, 2003; Hoffman and Shaqfeh, 2007), there have been almost no computational studies of polymer solutions at finite concentrations undergoing mixed flow. Such flows are of significant interest in many practical applications, particularly in situations where there is a strong elongational component to the deformation, such as in inkjet printing or fibre spinning (Xu et al., 2007; Zettl et al., 2009). Consequently, obtaining a quantitative understanding of the rheological behaviour of non-dilute polymer solutions is not only of fundamental importance, but also vitally important for a number of practical applications. The aim of this paper is to develop a computational algorithm that enables the simulation of polymer solutions at finite concentrations subjected to planar mixed flows.

A challenging aspect of the development of an algorithm to simulate flows of finite-concentration polymer solutions is the implementation of appropriate periodic boundary conditions (PBCs), arising from the need to carry out simulations for an indefinitely long time. PBCs for planar shear flows and planar elongational flows have been developed by Lees and Edwards (1972) and Kraynik and Reinelt (1992), respectively, that enable computations to run indefinitely in these flows. These PBCs have, for example, been used by Bhupathiraju et al. (1996) and Todd and Daivis (1998) in nonequilibrium molecular dynamics (NEMD) simulations. Apart from NEMD simulations, these PBCs have also been implemented in a Brownian dynamics (BD) simulation algorithm by Stoltz et al. (2006) to simulate semidilute polymer solutions undergoing planar shear and planar elongational flows. In the context of planar mixed flows, Woo and Shaqfeh (2003) and Dua and Cherayil (2003) and Hoffman and Shaqfeh (2007) have carried out simulations of dilute polymer solutions using a BD algorithm. However, PBCs are *not* required in single chain simulations. Hunt et al. (2010) have derived suitable PBCs for planar mixed flows and implemented them in an NEMD algorithm, which has recently been applied in a couple of different contexts (Hartkamp et al., 2012, 2013).

While NEMD simulations have led to important insights into the behaviour of polymer melts in a variety of flows (Todd, 2001; Kröger M., 2004; Hajizadeh et al., 2014) they are not suited to simulating the large-scale and long-time behaviour of solutions of long polymer chains, because of the large number of degrees of freedom involved, and because such systems typically have relaxation times that are of the order of several seconds. Basically, the need to resolve the uninteresting motions of all the solvent molecules for extended periods of time makes NEMD simulations computationally expensive and inefficient. It is generally accepted that the best approach under these circumstances is to use mesoscopic simulation algorithms, such as the hybrid LB/MD (Ahlrichs and Dünweg, 1999), or MPCD (Gompper et al., 2009) algorithms, or Brownian dynamics, in which the solvent molecules are discarded altogether and treated implicitly.

To our knowledge, mixed flow PBCs have not been implemented in the context of a BD algorithm so far. In this paper, we discuss the implementation of PBCs for planar mixed flows in a multi-chain BD algorithm. In particular, we adapt the PBC implementation in NEMD by Hunt et al. (2010) to the context of BD. The development of such an algorithm will enable the simulation of the large-scale and long-time properties of polymer solutions in industrially relevant flows at industrially relevant concentrations.

To illustrate the capabilities of the BD algorithm developed here, we present some preliminary results on the planar mixed flow of non-dilute polymer solutions. Shaqfeh and coworkers (Hur et al., 2002; Woo and Shaqfeh, 2003; Hoffman and Shaqfeh, 2007) have shown that the mixedness parameter χ is essential to understanding the nature of polymer behaviour in mixed flows. For instance, χ is a key parameter in determining the existence of the phenomenon of coil-stretch hysteresis (de Gennes, 1974; Schroeder et al., 2003, 2004). Here, we study the influence of flow type χ, and flow strength $\dot{\Gamma}$ on the viscosity in planar mixed flows, using the definition of viscosity introduced by Hounkonnou et al. (1992). Additionally we show that, as in the case of dilute solutions, there exits a critical value, χ_c, below which the flow is shear dominated, while being extension dominated for $\chi > \chi_c$. We find that the concentration of the polymer solution influences χ_c, and consequently the nature of the flow.

The plan of the paper is as follows. Different forms of the velocity gradient tensor for planar mixed flows are discussed in Section 2. In Section 3 we discuss the governing equations of the BD algorithm (Section 3.1), the implementation of PBCs in planar mixed flows (Section 3.2), the definition of various macroscopic properties (Section 3.3), and the validation of the BD algorithm by comparison with known results (Section 3.4). In Section 4, the results of simulations of FENE dumbbells are presented, and the influence of flow strength and mixedness parameter on polymer size and viscosity is discussed. The central conclusions of this work are summarized in Section 5.

2. Planar mixed flows

The velocity gradient tensor for planar shear flow (PSF) in matrix form is (Bird et al., 1987a)

$$(\nabla \boldsymbol{v})_{\mathrm{PSF}} = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{1}$$

where $\dot{\gamma}$ is the shear rate. The simplicity of planar shear flows has motivated many studies that have compared experimental observations with simulation predictions (Larson, 1999; Hur et al., 2000; Hsieh and Larson, 2004; Schroeder et al., 2005).

The velocity gradient tensor for planar elongational flow (PEF) is given by (Bird et al., 1987a)

$$(\nabla \boldsymbol{v})_{\mathrm{PEF}} = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{2}$$

where $\dot{\epsilon}$ is the elongational rate. Planar elongational flows occur in many industrial processes, and are generally difficult to study using computer simulations and experimental techniques, since in PEF, fluid elements are stretched exponentially with time in one direction while being contracted in the perpendicular direction (Bird et al., 1987a), leading to a very short span of time in which to observe the phenomena of stretching.

In planar mixed flow (PMF), the velocity gradient tensor has the following form (Fuller and Leal, 1981; Hounkonnou et al., 1992; Hoffman and Shaqfeh, 2007; Hunt et al., 2010):

$$(\nabla \boldsymbol{v})_{\mathrm{PMF}} = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ \dot{\gamma} & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{3}$$

which is referred to as the *canonical form* (Hunt et al., 2010). The expanding direction is along the x-axis and the contracting direction is along the y-axis, with elongational field strength $\dot{\epsilon}$, while the shear gradient is along the y direction, with shear field strength $\dot{\gamma}$. It follows that the expansion axis is always parallel to the x-axis, but the contraction axis is along the direction of one of