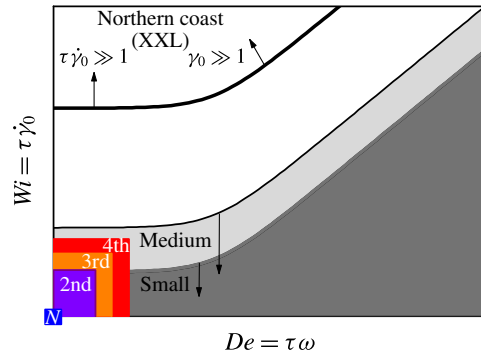# Focus on **Fluids**

Predictions for the northern coast of the shear rheology map: XXLAOS

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A new paradigm of rheological characterization, oscillatory simple shear with infinite forcing amplitudes, is introduced by Khair (*J. Fluid Mech.*, vol. 791, 2016, R5). This pushes the technique of large-amplitude oscillatory shear (LAOS) to have two extremely large amplitudes (both strain-rate and strain), which we might call XXLAOS. Model-specific analytical predictions are derived for a suspension of nearly spherical rigid particles subject to Brownian rotational diffusion. The work illuminates a new regime of rheological characterization that may serve as a distinct proving ground for constitutive model selection and for probing the flow physics of rheologically complex fluids.

Key words: mathematical foundations, rheology, viscoelasticity

1. Introduction

Rhelogically complex fluids have non-trivial constitutive equations for the stress tensor $\boldsymbol{\sigma}$, which responds to the time-dependence and forcing amplitude of the flow. To probe the complexity of the stress tensor $\boldsymbol{\sigma}$, simple velocity fields $\boldsymbol{v}$ are typically used. Flows that evoke transient and/or nonlinear stress responses help in inferring underlying physics and comparing experiments to models.

The most common rheological characterization flow is laminar, homogeneous, simple shear with a single velocity component $v_x = \dot{\gamma}(t)y$. Although the scheduling of $\dot{\gamma}(t)$ could be arbitrary, sinusoidal oscillations of the form $\dot{\gamma}(t) = \dot{\gamma}_0 \cos(\omega t)$ have proven very useful. With finite forcing amplitudes that produce a nonlinear response, the technique is called large-amplitude oscillatory shear (LAOS) characterization (for a review see Hyun *et al.* (2011)). Sinusoidal oscillations are experimentally convenient

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(avoiding step changes, allowing for signal averaging with multiple cycles) and allow for decomposition of energy storage and loss concepts.

The Pipkin map (Pipkin 1972) organizes the two-dimensional response of time-dependent and amplitude-dependent rheological complexity (see the title figure, adapted from Bharadwaj & Ewoldt (2014)). For oscillatory characterization, the Pipkin map is defined by the flow reversal frequency ω (abscissa) and flow amplitude (ordinate), e.g. strain-rate amplitude $\dot{\gamma}_0$ or strain amplitude $\gamma_0 = \dot{\gamma}_0/\omega$. The coordinates can be made dimensionless with a characteristic stress relaxation time τ of the material, in which case the Deborah number $De = \tau\omega$ and the Weissenberg number $Wi = \tau\dot{\gamma}_0$ define the abscissa and ordinate, respectively (whereas $De = \tau\omega$ determines the viscoelastic features, the forcing amplitude determines the nonlinearity, e.g. shear thinning is observed when Wi is sufficiently large).

All Newtonian fluids occupy only a single point of the Pipkin map, the origin, since the relaxation time $\tau \to 0$ for Newtonian fluids. We might call this the 'southwest' corner of the Pipkin space (the lower left). Various limits can be taken to explore the extreme edges, or coasts, around the Pipkin map. Three familiar limits were described by Pipkin (1972). Along the south coast (infinitely small forcing) is the limit of linear viscoelasticity, the west coast ($De \to 0$) is nonlinear purely viscous, and the east coast ($De \to \infty$) is the limit of nonlinear purely elastic.

Of the interior region, Pipkin remarked that 'Nothing very systematic is known...'. Indeed, the full map, and the interior region specifically, boasts a zoo of responses, bringing experimental challenges, data reduction challenges and a broad range of model-specific predictions (Pipkin 1972; Giacomin & Dealy 1993; Hyun *et al.* 2011).

The northern coast of the Pipkin map has never been considered as a limit to explore, until now. Khair (2016) takes the limit of infinite forcing amplitudes as a key paradigm, introducing a new concept for LAOS flow characterization. As Khair shows, both the strain-rate amplitude and strain amplitude must approach infinity to achieve this limit. Since two amplitudes must be 'extra' large, we might use the term extra-extra-large-amplitude oscillatory shear (XXLAOS) to identify the regime. Using a paradigmatic model of dilute nearly spherical colloids, an analytical result is derived. This is mathematically non-trivial; although forcing amplitudes are extremely large, the forcing oscillates and thus also goes through zero. These 'turning regions' require special mathematical attention. Khair shows us the way, deriving the results, and setting the stage for experimental validation and analytical solutions to other constitutive models in this limit.

2. Overview

The limit of strongly nonlinear LAOS, or XXLAOS, is novel and a bit weird: the shear rate oscillates between positive and negative 'infinity', but in finite time! The response depends on how quickly (ω) the flow reverses. Of course, the forcing amplitude does not actually need to reach infinity. Concepts of limits, dimensionless groups and comparison of terms allow for the limit to be taken.

Unique challenges exist for XXLAOS compared to other limits. For example, the limit of small amplitude oscillatory shear (SAOS), the linear viscoelastic regime, is defined by $\dot{\gamma}_0 \to 0$ and $\gamma_0 \to 0$; in this case the flow strength is always small, anywhere in the oscillatory cycle. Similarly, an expansion to asymptotically nonlinear forcing amplitude, sometimes called medium-amplitude oscillatory shear (MAOS), has oscillatory signals that are also sufficiently small throughout the entire oscillation. In contrast, the XXLAOS regime is defined by the flow forcing being extremely large,

yet since the flow reverses, the instantaneous strain rate $\dot{\gamma}(t)$ and accumulated strain $\gamma(t)$ also take values of zero. These somewhat contradictory limits require proper mathematical treatment.

The successful mathematical approach is to use a 'multi-scale' or 'two-timing' expansion of the response. Importantly, this requires WKBJ theory (Hinch 1991) to identify a suitable 'fast' timescale. With this approach, the core regions of high shear rate and the turning regions with near-zero shear rate can be individually solved and reconciled.

The key result of Khair (2016) is that an analytical solution is derived for this strongly nonlinear LAOS limit for the entire stress tensor $\boldsymbol{\sigma}$. Fast oscillations are observed in the high shear rate portions of the curve as the particles are advectively rotated by the vorticity of the flow (Jeffery orbits). In what Khair calls the turning regions, the shear rate is low (near zero), and the dynamics are dominated by rotational diffusion. The analytical results rationalize the timescales of the observed dynamics and provide explicit predictions of scaling with respect to the Weissenberg number $Wi = \tau \dot{\gamma}_0$ and Deborah number $De = \tau \omega$ (i.e. β and α, respectively, in Khair's notation).

The predicted hysteresis curves (a.k.a. Lissjous curves) are perhaps the most unique in the published literature. They exhibit multiple self-intersections due to fast oscillations on timescales much smaller than the periodic timescale $T = 2\pi/\omega$. This is a provocative prediction, although it is consistent with the predicted response in start-up of steady shear of the same model (Leal & Hinch 1972), and experimental rheo-optics observations of suspensions of spheroidal particles. This raises several interesting questions: is this a general feature of all models in this limit? Even if a model does not predict 'fast' oscillations during the periodic cycle, is it true that the response in the turning region could still dominate the rheological response, as observed with the Wi scaling here?

The frequency dependence is not discussed in detail by Khair, but the predictions are contained in the analytical solution. It will prove very interesting to compare the frequency dependence in this regime with other limits in the Pipkin space, in particular the small- and medium-amplitude regimes. In SAOS, there would be an analogy to frequency-dependent signatures of the linear viscoelastic moduli $G'(\omega)$ and $G'(\omega)$, and for MAOS an analogy to the four measurable asymptotically nonlinear shear material functions $[e_1](\omega)$, $[e_3](\omega)$, $[v_1](\omega)$ and $[v_3](\omega)$, which can be used to compare and contrast different material and constitutive models (Bharadwaj & Ewoldt 2015). Similar comparisons in the strongly nonlinear LAOS regime may further help distinguish materials and constitutive models while still being accessible to analytical solutions.

Some context should be noted regarding other research efforts in LAOS characterization. Khair's contribution here is not a new way to describe LAOS oscillatory signals; in that category of signal processing are Fourier transforms, Chebyshev polynomials and various local measures (Ewoldt, Hosoi & McKinley 2008; Hyun *et al.* 2011; Rogers 2012). Rather, Khair gives a paradigm of using the limit of 'infinite' forcing amplitudes for LAOS characterization. This is a specific region of the Pipkin map, complementing other limits such as SAOS and MAOS. Indeed, these results may inspire a trend of solving other model equations to see how similar or different rheological fingerprints may be in this limit.

3. Future

Several new questions arise with the concept of infinite forcing amplitude as a distinct regime for oscillatory characterization.

Experimentally, there are questions general to this technique and specific to these model predictions. Are experiments possible in this regime? A key challenge is the inherent assumption of negligible fluid inertia. Experimental forcing is typically imposed by boundary-driven flow and must deal with viscoelastic shear waves (Schrag 1977). Additional experimental challenges at extremely large amplitude (even modest amplitude) include edge fracture, slip at the boundary or slip within the fluid sample, all of which violate the assumptions of homogeneous simple shear flow. It may be possible to surmount these challenges with carefully chosen materials with long relaxation timescales and small critical strains, or by using smaller length-scale microrheology (either small confinement or small embedded probe microrheology).

If experiments are possible, then there are specific questions related to the model predictions of Khair (2016): can the core regions of fast oscillations be observed? What of the Weissenberg-number scaling or the frequency-dependent signatures? More generally, how different are these XXLAOS rheological signatures for different material systems?

There are more questions regarding theoretical understanding. How different are the responses for different constitutive models in this limit? Is anything general, as it is in the low Deborah number limit for SAOS and MAOS (Bharadwaj & Ewoldt 2014)? Are analytical results achievable for many models? For those that are, the mathematical challenges may have a similar flavour to the multi-scale expansions demonstrated here by Khair (2016), but this remains to be explored.

More broadly, the concept of strongly nonlinear oscillations may be applicable to other fields beyond rheology, e.g. dielectric, electrochemical, magnetic and mechanical systems. Analogous Pipkin spaces may have their own northern coasts in the limit of infinite forcing amplitude. These curious questions can now be asked, and some guidance provided, thanks to the work of Khair.

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