

## Spreading of liquids on solid surfaces: pure fluids

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Dynamic wetting is a key phenomenon in many natural and technological processes. The impact of non-Newtonian behavior in wetting is important not only because many fluids in technological use are clearly non-Newtonian but, more importantly, because fluids that are nominally considered Newtonian exhibit non-Newtonian behavior in the high-shear environment next to a moving contact line.

Moving contact line flows have the unique feature that they subject the fluid to divergent deformation rates as the distance to the contact line decreases. When a fluid whose constitutive relation depends on a characteristic time scale enters the region where the inverse deformation rates are comparable to its time scale, the fluid behavior undergoes a qualitative change from that in the "bulk" where the molecular process associated with that time scale is fully relaxed. Since real fluids all have a set of characteristic times governing their internal dynamics, it is natural to wonder whether the flow near a contact line can be properly described using a Newtonian model which does not contain any characteristic time scale. Our results suggest that fluids that appear Newtonian in conventional rotational rheometry can show deviations from the wetting behavior of purely Newtonian fluids, likely because of their non-Newtonian behavior near the contact line.

Polymeric fluids, including polymer melts and solutions, exhibit two broad classes of non-Newtonian behavior, viz., shear-thinning and elasticity. Usually these two behaviors appear simultaneously. We have prepared two sets of fluids, each one's rheology dominated by either shear-thinning or elasticity. Aqueous xanthan gum solutions shear thin in rotational rheology

with undetectable normal stress differences –indicating minimal to no elasticity. Fluids whose characteristic shear-thinning length scale,  $U/\dot{\gamma}_c$  (where  $\dot{\gamma}_c$  is the lower critical shear rate and  $U$  the spreading velocity), is comparable to the length scale where viscous deformation is significant, exhibit less viscous deformation near the contact line than a Newtonian fluid with the same zero-shear viscosity  $\eta_0$ . When the apparent dynamic contact angle,  $\theta_d$ , is plotted versus Capillary number  $Ca$  ( $\equiv U\eta_0/\sigma$ , where  $\sigma$  is surface tension), the rate of variation is lower than that for Newtonian fluids –characterized by the well-known power law  $\theta_d \sim Ca^{1/3}$ . This is explained by realizing that near the solid where shear rates are highest, the fluid shear thins. As a consequence, the solid is less effective in dragging fluid away from the contact line region, and less fluid per unit time must be injected back into the contact line along the free surface. This, then, demands a smaller pressure gradient along the free surface than in the Newtonian fluid, causing the viscous bending to be decreased and, with that, the dynamic contact angle of the shear-thinning liquid to be smaller than that of the Newtonian liquid at each  $Ca$ .

The dynamic wetting of a solution of polyethylene oxide (PEO) shows enhanced curvature of the liquid-vapor interface near the contact line, while its rheology shows both shear thinning and elasticity. These measurements motivated us to examine the dynamic wetting of a fluid with elasticity-dominated rheology and minimal shear thinning. We use a measurably elastic Boger<sup>1</sup> fluid made of polystyrene (PS) oligomer doped with a small amount of high molecular weight PS. In contrast to the shear thinning of xanthan gum solutions, these fluids show greater viscous bending than a Newtonian fluid with the same shear viscosity, strongly suggesting that elasticity enhances the viscous bending. When we examine wetting by the base

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<sup>1</sup> Boger Fluids are constant shear viscosity fluids that exhibit first and second normal stress differences –indicating elasticity.

PS used to produce the Boger fluid, we still observe enhanced viscous bending even though the longest relaxation times in the PS are more than an order of magnitude less than those in the Boger fluid. While both these fluids show enhanced viscous deformation near the contact line, only the viscous deformation of the PS base farther from the contact line agrees with that seen in a Newtonian fluid under similar flow conditions. This causes the functional form of  $\theta_d$  versus  $Ca$  for the PS base to remain unperturbed. We observe similar behavior for a Boger fluid based on polyisobutylene (PIB) and the base PIB. All these results clearly indicate that elasticity causes higher normal stresses on the free surface –and hence, higher apparent contact angle– than in a Newtonian fluid with the same zero-shear viscosity, but that the molecular modes with the longest relaxation times do not dominate the enhanced deformation.

Acknowledgement: We acknowledge the work of Yue Suo, Gita Seevaratnam, and the support of NASA.