



On the conformational state of molecules in molecularly thin shearing films

In their recent PNAS article, Rosenhek-Goldian et al. (1) write: “Intermittent sliding (stick–slip motion) between solids . . . even in the presence of lubricants, is believed to occur by shear-induced fluidization of the lubricant film (slip), followed by its resolidification (stick).” The authors describe their results on the stick–slip of a commonly studied liquid, octmethylcyclotetrasiloxane (OMCTS), whose soft, quasi-spherical molecules have a diameter of ~1 nm, and measured no dilatancy at the ~0.1-nm resolution level during rapid slips, and conclude “. . . that, in contrast to accepted and long-standing belief, shear melting (fluidization) of thin lubricant layers does not occur in stick–slip sliding . . .” and “. . . that other mechanisms, such as intralayer slip within the lubricant film, or at its interface with the confining surfaces, may be the dominant dissipation modes” (1). Rosenhek-Goldian et al. suggest that these two alternative mechanisms may be the ones that occur in general with other liquid lubricant systems.

Interpreting stick–slip sliding, and lubricated sliding in general, has long been attributed to exactly one (or more) of the three mechanisms proposed (see, for example, figure 18.10 in ref. 2). Moreover, by the same

reasoning these “other mechanisms” should also involve dilatancy, so that the finding of Rosenhek-Goldian et al. (1) seems to rule out these interpretations as well, if we accept the reason given for ruling out shear melting.

Dhinojwala et al. (3) measured dilatancy at the onset of slip in films of a variety of different fluids, including OMCTS, alkanes, other small molecules, branched hydrocarbons, and polymer fluids, and discussed “. . . the generality of the dilation effect . . .” [see also Demirel and Granick (4)]. At about the same time, Drummond and Israelachvili (5) measured dilatancy during sliding of branched hydrocarbon liquids, such as squalene; and—for more complex liquids, such as linear or branched hydrocarbons or polymer liquids—suggested possible interpretations, including shear alignment (shear thinning), entanglement-disentanglement effects, and entry of fluid from the surrounding “bulk reservoir” into the gap.

In general, however, liquids do not always expand on melting, and some—like water—contract significantly. Thus, dilatancy alone (or the lack of it) cannot be a sufficient criterion for concluding the changes in molecular reorganization that occur in thin

lubricating films during steady or stick–slip sliding.

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1 Rosenhek-Goldian I, Kampf N, Yeredor A, Klein J (2015) On the question of whether lubricants fluidize in stick–slip friction. *Proc Natl Acad Sci USA* 112(23):7117–7122.

2 Israelachvili J (2011) *Intermolecular & Surface Forces*, 3rd Ed, (Elsevier, Amsterdam).

3 Dhinojwala A, Bae SC, Granick S (2000) Shear-induced dilation of confined liquid films. *Tribol Lett* 9(1-2):55–62.

4 Demirel AL, Granick S (2002) Lubricated friction and volume dilatancy are coupled. *J Chem Phys* 117(16):7745–7750.

5 Drummond C, Israelachvili J (2000) Dynamic behavior of confined branched hydrocarbon lubricant fluids under shear. *Macromolecules* 33(13):4910–4920.

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The authors declare no conflict of interest.

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