lubricants

Comment

Comment on Neupert, T.; Bartel, D. Evaluation of Various Shear-Thinning Models for Squalane Using Traction Measurements, TEHD and NEMD Simulations. *Lubricants* 2023, *11*, 178

Scott Bair †

Georgia Institute of Technology, Center for High-Pressure Rheology, George W. Woodruff School of Mechanical Engineering, Atlanta, GA 30332-0405, USA; scott.bair@me.gatech.edu; Tel.: +1-404-226-8012

† Retired.

The field of EHL (elastohydrodynamic lubrication) may be the only one in science in which a model for shear-dependent viscosity would be evaluated by means other than viscometer measurements. The subject article [1] begins with "The accurate prediction of friction in highly loaded concentrated contacts is one of the most challenging aspects of thermal elastohydrodynamic (TEHD) simulation". The prediction of friction should not require a measurement of friction. That is a curve-fitting exercise which provides no insight concerning the rheology. The prediction of friction in a liquid film should be made from the properties of the liquid which may be measured outside of the contact. For nearly a century, viscometer measurements at EHL pressures [2] have indicated that the pressure response, which is slower than exponential, is restricted to the lowest pressures and becomes faster than exponential or at least exponential above an inflection pressure. This universal inflection is observed in squalane at about 700 MPa and 40 °C in Ref. [8] of the subject article and in Figure 1 below. The complete data set is shown, including some from Ref. [43] of the subject paper. That reference included experimental glass pressures and a piezoviscous function that is useful for extrapolation to very high pressures, shown as a Hybrid model [3] in Figure 1. The formulations based on the free-volume theory, such as Doolittle, which was used by the authors for one of the four shear-thinning models investigated, naturally display the inflection; however, they do not extrapolate as well as the Hybrid model.

One of the oils used by Johnson and Tevaarwerk [4] to generate traction curves was Shell Turbo 33, a mineral oil with a low inflection pressure at the experimental temperatures, so that the slower-than-exponential piezoviscous response did not appear [5]. In an influential paper, Houpert [6] proposed that if traction calculations were to reasonably reproduce experiments using the Eyring [7] assumption, then an extrapolation using the Roelands [8] equation should be used to understate the viscosity at high pressure instead of the real viscosity, which was known [5] at the time for Turbo 33. The authors of the subject article have adopted this procedure except that a different, but similar to Roelands, model is used, one that also cannot describe the high-pressure response. This is the Rodermund model [1] that is shown in Figure 1, where the viscosity is understated by more than a factor of three at the highest pressure. Using the Hybrid model for extrapolation, the error is an order of magnitude at 1500 MPa. A major difference from Houpert is that Houpert did not justify the use of an inaccurate correlation by claiming, as the authors have, that "On the basis of the available measurement values, an interpolation fitting was carried out so that all data are matched as well as possible". It is clear from Figure 1 that the data and the correlation do not match.

check for updates

Citation: Bair, S. Comment on Neupert, T.; Bartel, D. Evaluation of Various Shear-Thinning Models for Squalane Using Traction Measurements, TEHD and NEMD Simulations. *Lubricants* 2023, *11*, 178. *Lubricants* **2023**, *11*, 393. https://doi.org/10.3390/lubricants11090393

Received: 26 June 2023
Revised: 8 August 2023
Accepted: 8 September 2023
Published: 12 September 2023

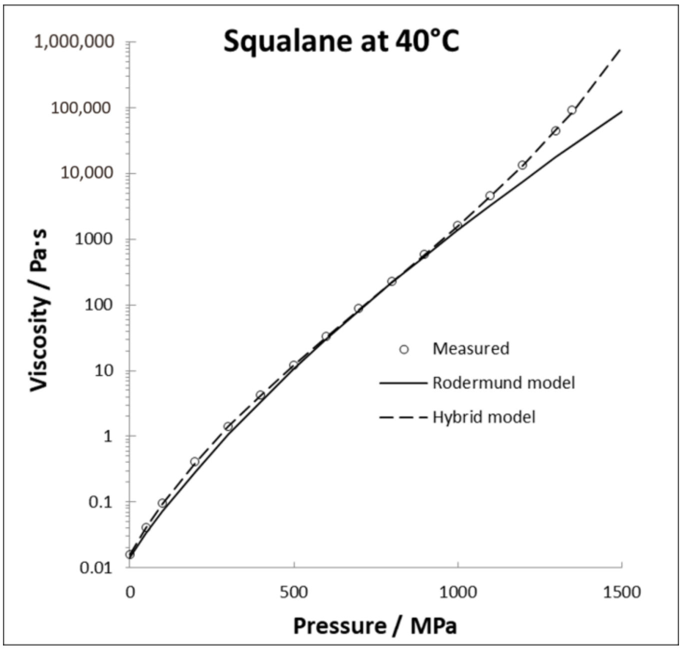

Figure 1. The viscosity of squalane measured at 40 °C compared with a model useful for extrapolation and the presentation in the subject article.

Reference liquids such as squalane are useful in EHL research because many of their high-pressure properties are known, but only if use is made of these properties. Experimental measurements of the thermal properties of squalane were made at Umeå University and reported in Ref. [43] of the subject article. From these data, the glass transition temperatures were clearly identified and fitted to the Oles and Rehage model to correlate the glass pressure with temperature. For example, the glass pressure at 20 °C is 1.25 GPa and at 40 °C, 1.54 GPa, according to Prentice et al. [9].

Using these published results, the only friction data in the subject article to have been entirely within the liquid state are those from the EHL2 tribometer. For the other tribometers, most friction measurements were obtained for the glassy, solid squalane. It is no surprise that the glass transition is not apparent in the traction curve. There can sometimes be little difference between traction curves with lubricant and without lubricant [10]. The subject article ignores what is known of the glass transition in squalane and makes the claim "Another possibility to determine the flow behaviour of lubricants under real conditions is to carry out traction measurements on model tribometers with very precise friction measurement". This cannot be true. It should not be possible to generate shear-thinning data on a solid.

The authors ignored the pressure dependence of viscosity at 21.5 °C in authors' Ref. [43], which would have shown that the viscosity was approaching the glass transition viscosity at 1.3 GPa [9], as shown in Figure 2.

The shear thinning observed in viscometers, which has been so successful in establishing the effects of shear-dependent viscosity on film thickness, should be used for evaluation of shear-thinning models because we have confidence in their accuracy. See Ref. [47] of the subject article for an example of a successful calculation of film thickness that could not have been done without such viscometer data. The Eyring model will not correctly reproduce the effect of shear-dependent viscosity on film thickness. See [11] and Ref. [13] of the subject article, among many others. The viscosity data in Figure 3 were generated with the viscometer that provided the correct film thickness calculations in [11]. For the conditions of the figure, the subject article specifies that the Eyring stress is 5.72 MPa and the low shear viscosity is 3.06×10^4 Pa·s using the Rodermund correlation.

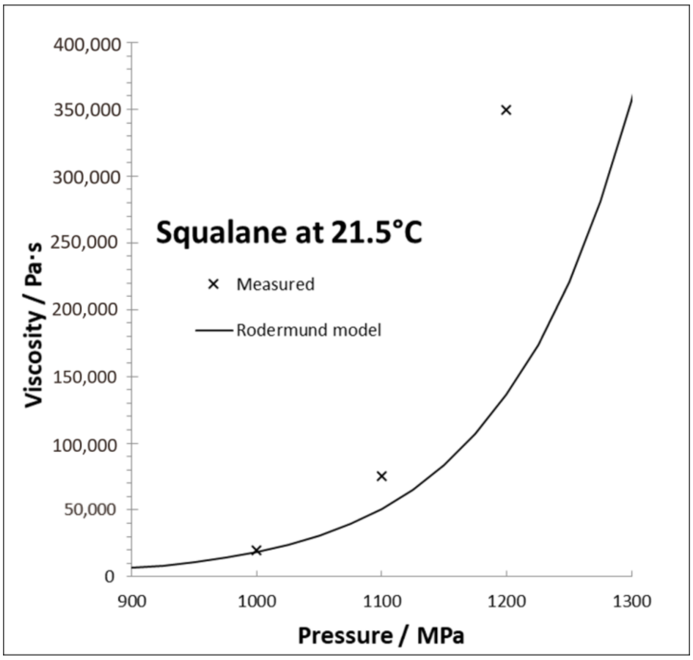

Figure 2. The viscosity of squalane measured at 21.5 °C compared with the model used for extrapolation in the subject article.

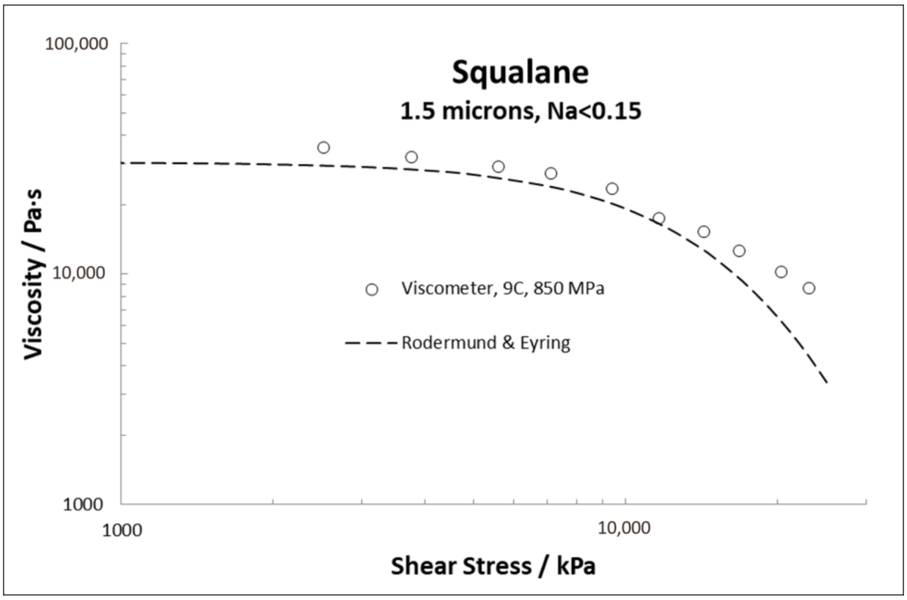

Figure 3. The viscosity of squalane measured in a pressurized thin-film Couette viscometer. The Eyring stress given in the subject article is 5.72 MPa.

Figure 3 shows what Henry Eyring understood by 1958 [7], that the sinh law is not accurate over a wide range of shear stress. This viscometer can produce a flow curve that fits the Eyring equation by choosing conditions for which the Eyring stress is attained when the Nahme–Griffith number is 0.3. This is because the Eyring sinh law is a relation for the thermally softened viscosity arising from viscous dissipation [12]. The Eyring curve in Figure 3 should be recognizable as a thermal artifact to those familiar with such measurements. A viscometer, operated correctly, provides the evaluation of shear-thinning models that obviates any need for the subject article.

The correlation used by the authors of the subject article understates the viscosity at high pressure in a way that favors a particular interpretation of the traction data. They state, "While the measurement in rheometers indicates solidification for very high pressures, our investigations show that the assumption of a further degressive curve, in connection with the available shear-thinning models, leads to better agreements with the traction measurements than a progressive approach". However, no organic liquid possesses the previtreous, piezoviscous response employed in this work, the degressive curve. The faster-than-exponential pressure response of the progressive curve, which was omitted, is the universal previtreous response of all supercooled liquids [13,14] and does not invoke solidification but is necessary for the prediction of minimum film thickness. The one conclusion to be drawn from the subject article is that the Eyring sinh law cannot accurately predict traction without altering the piezoviscous response in an arbitrary way.

Conflicts of Interest: The author declares no conflict of interest.

References

1. Neupert, T.; Bartel, D. Evaluation of Various Shear-Thinning Models for Squalane Using Traction Measurements, TEHD and NEMD Simulations. *Lubricants* **2023**, *11*, 178. [CrossRef]
2. Bridgman, P.W. The Effect of Pressure on the Viscosity of Forty-Three Pure Liquids. *Proc. Amer. Acad.* **1926**, *61*, 57–99. [CrossRef]
3. Thoms, E.; Grzybowski, A.; Pawlus, S.; Paluch, M. Breakdown of the Simple Arrhenius Law in the Normal Liquid State. *J. Phys. Chem. Lett.* **2018**, *9*, 1783–1787. [CrossRef] [PubMed]
4. Johnson, K.L.; Tevaarwerk, J.L. Shear behaviour of elastohydrodynamic oil films. *Proc. R. Soc. Lond. A Math. Phys. Sci.* **1977**, *356*, 215–236.
5. Bair, S.; Winer, W.O. Some observations in high pressure rheology of lubricants. *J. Lubr. Technol.* **1982**, *104*, 357–364. [CrossRef]
6. Houpert, L. New results of traction force calculations in elastohydrodynamic contacts. *J. Tribol.* **1985**, *107*, 241–248. [CrossRef]
7. Ree, F.; Ree, T.; Eyring, H. Relaxation theory of transport problems in condensed systems. *Ind. Eng. Chem.* **1958**, *50*, 1036–1040. [CrossRef]
8. Roelands, C.J.A. Correlational Aspects of the Viscosity-Temperature-Pressure Relationship of Lubricating Oils. Ph.D. Thesis, Technical University of Delft, Delft, The Netherlands, 1966.
9. Prentice, I.J.; Liu, X.; Nerushev, O.A.; Balakrishnan, S.; Pulham, C.R.; Camp, P.J. Experimental and simulation study of the high-pressure behavior of squalane and poly-α-olefins. *J. Chem. Phys.* **2020**, *152*, 074504. [CrossRef] [PubMed]
10. Bair, S.; Kotzalas, M. The contribution of roller compliance to elastohydrodynamic traction. *Tribol. Trans.* **2006**, *49*, 218–224. [CrossRef]
11. Hooke, C.; Šperka, P.; Bair, S.; Morales-Espejel, G.E. A comparison of measured film thicknesses with quantitative predictions from an elastohydrodynamic, perturbation analysis at high slide-roll ratios. *Proc. Inst. Mech. Eng. Part J J. Eng. Tribol.* **2021**, *235*, 870–880. [CrossRef]
12. Lower, G.W.; Walker, W.C.; Zettlemoyer, A.C. The rheology of printing inks. II. temperature control studies in the rotational viscometer. *J. Colloid Sci.* **1953**, *8*, 116–129. [CrossRef]
13. Floudas, G.; Paluch, M.; Grzybowski, A.; Ngai, K. *Molecular Dynamics of Glass-Forming Systems: Effects of Pressure*; Springer Science & Business Media: Heidelburg, Germany, 2010; Volume 1, pp. 7–8.
14. Drozd-Rzoska, A. Pressure-related universal previtreous behavior of the structural relaxation time and apparent fragility. *Front. Mater.* **2019**, *6*, 103. [CrossRef]