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NUMERICAL MODELING OF ZDDP-INDUCED RHEOLOGICAL CHANGES IN POLYMOLECULAR ADSORPTION LAYERS OF THIN LUBRICATING FILMS

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Abstract: The rheological response of a confined lubricant film is examined using a one-dimensional numerical model in which viscosity varies continuously between the two solid boundaries and the central mobile region. The formulation combines an exponential representation of the near-surface viscosity profile with symmetric, immobile interfacial layers. An L-AN 32 mineral oil is adopted as a reference medium, with its bulk dynamic viscosity set to 0.028 Pa·s as a prescribed model input. Three parameter sets are used to represent weak, intermediate and pronounced interfacial structuring; these sets are illustrative and are not fitted to measurements or assigned to specific ZDDP concentrations. The effective viscosity is obtained from the harmonic meaning of the local viscosity across the mobile film. Calculations cover total film thicknesses from 20 to 2000 nm, while a separate sensitivity study examines the influence of the adsorption decay length. The calculations indicate that interfacial structuring has its greatest relative effect in the thinnest films. As the gap widens, the contribution of the central, near-bulk region increases and the effective viscosity tends towards the prescribed bulk value. The work provides a parametric assessment of how assumed interfacial rheological properties influence the through-thickness effective viscosity; it does not quantify ZDDP concentration effects or predict friction, pressure distribution, or load capacity.

Keywords: thin lubricating film, polymolecular adsorption, L-AN 32 oil, adsorption layer, effective viscosity, numerical modeling, rheological behaviour

1. INTRODUCTION

Lower-viscosity lubricants are increasingly considered in efforts to reduce viscous losses in engines. A reduction in bulk viscosity, however, can also decrease the thickness of the separating film and increase the importance of interfacial phenomena in highly loaded contacts. When the lubricant gap becomes very small, its rheological response may no longer be represented adequately by a single bulk-viscosity value.

Studies of confined liquids have reported changes in molecular organization, flow behavior and apparent viscosity as the separation between solid surfaces approaches molecular dimensions. Hu and Granick [1] investigated viscoelastic dynamics in confined polymer melts, while the review by Xiang et al. [2] summarizes surface-force measurements and interaction mechanisms relevant to soft thin films under confinement. Together, these works demonstrate why surface interactions and confinement need to be considered when describing the response of very thin liquid layers. A separate but related issue concerns anti-wear additives. ZDDP is known to form protective tribochemical films on rubbing surfaces. Spikes [7] review the mechanisms of ZDDP action, including adsorption and the development of phosphate-based tribofilms. Ueda and Spikes [8] further show that tribofilm growth and removal can occur concurrently and depend on additive chemistry and operating conditions. These studies concern tribochemical film formation; they do not establish the numerical parameters of the interfacial viscosity profile considered in the present work. The earlier paper by Drach et al. [9] provides the direct background for the authors' broader modelling approach. The present paper focuses specifically on a

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controlled parametric calculation of the equivalent viscosity for prescribed interfacial properties, without claiming to predict ZDDP concentration effects or experimental friction.

2. LITERATURE REVIEW

The rheological behavior of confined liquid films has been investigated using both experimental and theoretical approaches. Hu and Granick [1] reported viscoelastic effects in polymer melts under confinement, while Xiang et al. [2] reviewed the principal surface-force measurement techniques, including the surface forces apparatus and atomic force microscopy. Their review highlights the role of intermolecular interactions, film properties and operating conditions in determining adhesion, friction and lubrication behavior. These studies provide a physical basis for considering spatial variations in the rheological properties of nanometer-scale lubricant films.

Several theoretical models have been developed to account for the influence of solid boundaries on thin-film lubrication. Tichy [4] introduced a surface-layer model in which the near-wall region is treated as a distinct layer with properties different from those of the bulk lubricant. Qu et al. [3] proposed an equivalent-viscosity model based on adsorption theory to describe the effect of surface interactions on thin-film lubrication. A related approach was developed by Ono [5], who incorporated a high-viscosity surface layer into modified Reynold's equations. Although these formulations differ in their assumptions and applications, they demonstrate that interfacial regions can substantially influence the effective rheological response of confined lubricants. Unlike models that explicitly solve the pressure distribution or bearing performance, the present study is limited to evaluating the effective viscosity through the thickness of a prescribed non-uniform viscosity field.

The adsorption-potential concept introduced by Polanyi [6] provides a theoretical basis for describing changes in molecular potential with distance from a surface. In the present study, this concept is used as a phenomenological justification for representing the near-surface viscosity variation by an exponentially decaying function. The model does not calculate adsorption isotherms, molecular coverage or chemical reaction kinetics; instead, it describes the rheological response through prescribed model parameters.

The role of anti-wear additives, particularly zinc dialkyldithiophosphate (ZDDP), represents a related aspect of boundary lubrication. Spikes [7] reviewed the mechanisms of ZDDP action, including its interaction with surfaces and the formation of protective phosphate-based tribofilms. Ueda and Spikes [8] experimentally investigated tribofilm formation and removal, demonstrating the dynamic nature of these processes. These studies address the chemical mechanisms and evolution of protective surface films rather than the effective viscosity of the mobile lubricant layer. Accordingly, the adsorption scenarios considered in the present work are prescribed rheological cases and should not be interpreted as quantitatively representing specific ZDDP concentrations or their effects.

The present study builds on the authors' earlier work [9] by refining the scope of the numerical analysis and examining the sensitivity of effective viscosity to the main parameters governing the interfacial rheological profile. Specifically, the analysis considers near-interface viscosity, characteristic decay length and immobile-layer thickness, and evaluates their combined influence over a range of total film thicknesses. The contribution of this study is a systematic parametric assessment based on an explicitly defined mathematical model, rather than an experimental evaluation of ZDDP performance.

3. THEORETICAL MODEL AND NUMERICAL CALCULATION METHODOLOGY

The present model considers a confined lubricant film between two nominally smooth, chemically homogeneous solid surfaces. The idealized contact geometry and the assumed structure of the confined lubricating film are shown in Figure 1.

Adsorption layers of prescribed properties are assumed to form symmetrically at both surfaces. The model describes a spatially varying viscosity in the mobile region; it does not solve the Reynolds pressure equation, predict the load-carrying capacity, or resolve asperity contact and tribochemical film growth.

A lubricant layer of total thickness h is considered between two parallel solid boundaries. Each boundary is assumed to be covered by an immobile interfacial region of thickness hs, leaving a central mobile region in which shear flow is represented. The idealised arrangement and the coordinate system are illustrated in Figure 1. The two

interfacial regions are taken to have identical properties, so that the viscosity field is symmetric about the mid-plane.

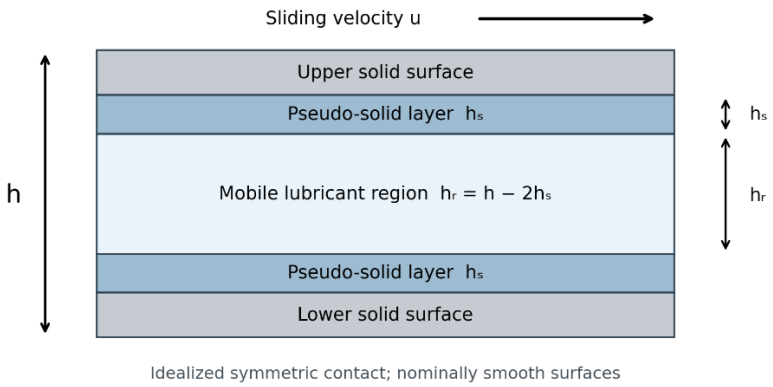

Figure 1. Calculation scheme of a thin lubricating film with symmetric adsorption layers

Within the mobile portion of the gap, the local dynamic viscosity is prescribed as a function of distance from the nearest interfacial boundary. An exponential transition is adopted because it allows the near-wall value to relax continuously towards the bulk-fluid value over a characteristic distance:

$$\mu(\zeta) = \mu_s + (\mu_0 - \mu_s) \cdot \left[1 - \exp\left(-\frac{\zeta}{l_h}\right)\right], \tag{1}$$

In this expression, ζ denotes the distance from the edge of the immobile region, μ_0 is the bulk dynamic viscosity, μs is the viscosity assigned at the mobile-region boundary, and lh is the decay length governing the spatial transition.

The surface-related contribution is represented by an exponential transition between the near-interface viscosity μs and the bulk value μ0. The parameter lh controls the rate at which the influence of the boundary decays into the liquid. It is a model length scale, not a directly measured adsorption-layer thickness. Values reported for confined liquids and additive-containing systems vary with chemistry and surface condition; therefore, the values used below are treated as scenario inputs.

For a symmetric contact with identical adsorption layers on both surfaces, the distance ζ is determined as

$$\zeta(z) = \min(z - h_s,\ h - h_s - z), \tag{2}$$

The coordinate ζ is measured from the edge of the immobile interfacial layer into the mobile liquid. Thus, μs is the viscosity assigned at the boundary between the mobile and immobile regions. It should not be interpreted as the viscosity at the solid substrate itself. The model treats the immobile layers as non-shearing regions and excludes them from the averaging operation.

Here z denotes the coordinate measured from the lower wall, h is the total separation, and hs is the prescribed thickness of each immobile interfacial region. The mobile domain is consequently bounded by z = hs and z = h − hs.

The effective thickness of the fluid film, in which hydrodynamic flow occurs, is

$$h_r = h - 2h_s. \tag{3}$$

For a fixed gap, prescribed sliding speed u and nominal area A, the model can provide an estimate of the viscous shear force in the mobile region using the effective viscosity. This expression is a simplified Couette-type estimate under the assumed geometry; it is not a calculation of the total friction force in a real mixed-lubrication contact.

An equivalent viscosity is introduced so that a uniform layer of thickness hr would produce the same shear response as the non-uniform mobile region. For layers arranged across the direction of the velocity gradient, the appropriate equivalent quantity is obtained through harmonic averaging:

$$\overline{\mu} = \frac{h - 2h_s}{\int_{h_s}^{h-h_s} \frac{dz}{\mu(z)}}. \tag{4}$$

The harmonic mean follows from the fact that the shear stress is transmitted through successive strata while the velocity gradient adjusts locally according to viscosity. Consequently, regions with lower viscosity contribute disproportionately to the total shear deformation.

For the symmetric exponential profile defined by Equation (1), the reciprocal-viscosity integral can be evaluated analytically under the stated assumptions:

$$\int_{h_s}^{h-h_s} \frac{dz}{\mu(z)} = \frac{2l_h}{\mu_0} \cdot \ln\left\{ \frac{\mu_0 \cdot \exp\left(\frac{h-2h_s}{2l_h}\right) - \mu_0 + \mu_s}{\mu_s} \right\}. \tag{5}$$

If the two interfacial profiles overlap strongly, or if the boundary conditions differ, the symmetric closed-form expression is no longer applicable. In those cases, the integral can be evaluated directly over the mobile domain using numerical quadrature.

Non-Newtonian rheology: the Carreau–Yasuda relationship can represent the gradual transition from low-shear Newtonian behavior to shear thinning, whereas the Eyring model describes stress-assisted molecular rearrangements and can be relevant to highly confined lubricants. The Carreau–Yasuda model was considered as a possible constitutive extension, but its shear-dependent response is not implemented in the numerical results reported here. The present calculations use the low-shear Newtonian limit; an Eyring comparison would require independently established activation parameters.

Numerical algorithm. (1) Prescribe μ0 and the three adsorption parameters μs, lh and hs; (2) select total film thickness h and verify h > 2hs; (3) calculate mobile thickness hr = h − 2hs; (4) evaluate the exponential viscosity profile at equally spaced nodes; (5) integrate 1/μ across the mobile region using the trapezoidal rule with 200 subdivisions; (6) calculate μeff = hr / ∫(1/μ) dz; (7) repeat over film thicknesses and decay lengths and plot the resulting sensitivities. The model inputs are illustrative and are not fitted to experimental friction measurements. A grid-refinement study is needed before claiming numerical convergence. The sequence of the numerical calculation and subsequent parametric analysis is summarized in Figure 2.

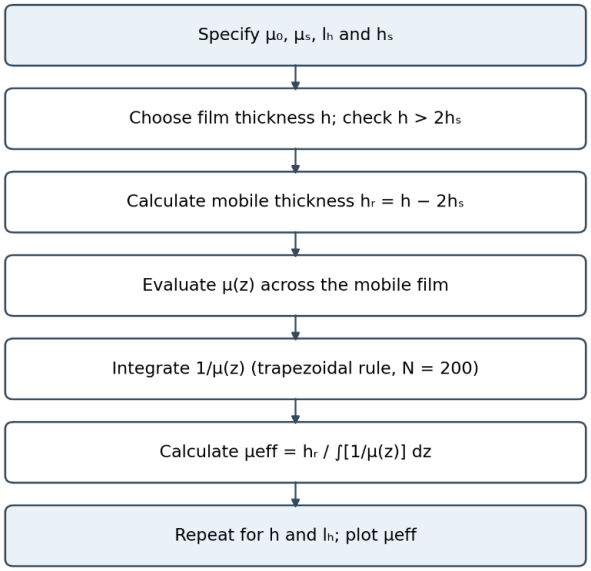

Figure 2. Flowchart of the numerical calculation of effective viscosity and parametric analysis.

The independent model inputs are the near-interface viscosity μs, the characteristic decay length lh and the thickness hs of each immobile interfacial region.

μ_s is the viscosity prescribed at the mobile/immobile interface;

l_h is the characteristic distance over which the surface-induced viscosity change decays;

h_s is the thickness assigned to the immobile interfacial region at each wall.

For the reference calculations, the bulk viscosity is set to μ0 = 0.028 Pa·s. This is a numerical input adopted for the L-AN 32 reference case, not a measurement reported for a specific oil batch. The three sets in Table 1 are selected to span progressively stronger interfacial structuring. The surfaces are idealized as smooth, rigid and chemically identical. Surface chemistry, roughness and oxide condition are not independently resolved; their possible influence is subsumed into the prescribed parameters. The model does not calculate pressure distribution, load sharing or the growth of a tribochemical film.

4. RESULTS OF NUMERICAL MODELING AND PARAMETRIC ANALYSIS

The numerical study examines how prescribed adsorption-layer properties affect the effective viscosity of a thin lubricating film. L-AN 32 is considered as a reference mineral oil, with an assumed bulk dynamic viscosity of $\mu_0 = 0.028$ Pa·s. This value is a modeling input and must not be interpreted as a measured property of a particular commercial product. Three illustrative adsorption scenarios are compared to separate the influence of interfacial structuring from any unverified concentration-dependent effects of ZDDP. The calculations use the exponential near-surface viscosity distribution and harmonic averaging introduced in Section 3. Symmetric adsorption layers are assumed at the two opposing surfaces, and the mobile-film thickness is $h_r = h - 2h_s$. The parameter sets are specified in Table 1; they are not obtained by fitting experimental friction curves.

Table 1. Prescribed parameters for illustrative adsorption scenarios (L-AN 32 reference oil).

Parameter	Weak	Moderate	Strong
Bulk viscosity μ_0, Pa·s	0.028	0.028	0.028
Near-surface viscosity μ_s, Pa·s	0.14	0.98	1.68
Decay length lh, nm	2.1	3.8	4.6
Pseudo-solid thickness hs, nm	0.8	1.4	1.9

The influence of total film thickness was evaluated between 20 and 2000 nm. The effective viscosity values calculated for the three parameter sets are summarized in Table 2 and plotted in Figure 3. All tabulated and graphical results are numerical model outputs rather than measurements.

Table 2. Calculated effective viscosity μeff (Pa·s) for different film thicknesses**.**

h, nm	Weak	Moderate	Strong
20	0.04349	0.28802	0.63840
50	0.03255	0.06390	0.11195
100	0.03007	0.03878	0.04601
200	0.02899	0.03245	0.03465
500	0.02839	0.02961	0.03030
1000	0.02819	0.02878	0.02910
2000	0.02810	0.02838	0.02854

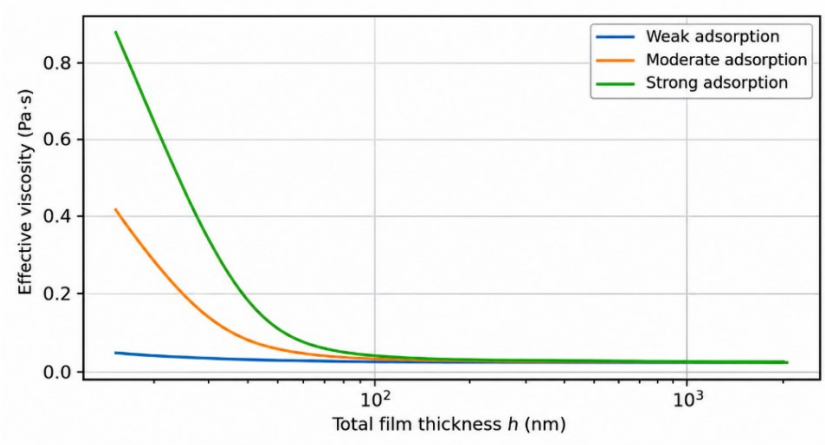

Figure 3. Effective viscosity versus total film thickness for weak, moderate and strong adsorption scenarios ($\mu_0 = 0.028$ Pa·s).

Calculated effective viscosity versus total film thickness for three prescribed adsorption scenarios; $\mu_0 = 0.028$ Pa·s. To distinguish the effect of adsorption-layer extension from that of surface viscosity, a separate sensitivity analysis was conducted by varying the characteristic decay length l_h while keeping $\mu_s = 0.98$ Pa·s and $h_s = 1.4$ nm. The calculated dependencies for three film thicknesses are shown in Figure 4.

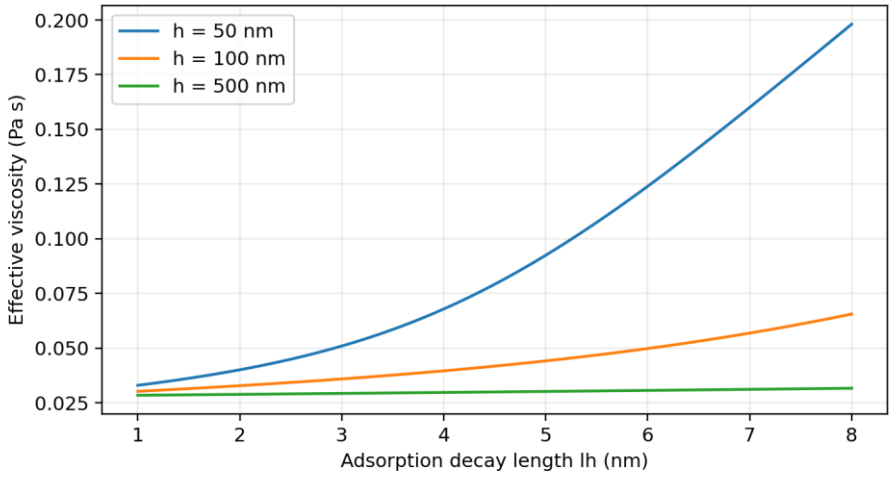

Figure 4. Influence of adsorption decay length l_h on effective viscosity at h = 50, 100 and 500 nm ($\mu_s = 0.98$ Pa·s; $h_s = 1.4$ nm).

Sensitivity of effective viscosity to adsorption decay length lh for h = 50, 100 and 500 nm (μs = 0.98 Pa·s; hs = 1.4 nm). Figure 4 isolates the effect of the characteristic adsorption length. Increasing lh increases the fraction of the film influenced by near-surface structuring, thereby increasing μeff. The absolute response is larger for thinner films; at larger h the less-viscous central region dominates the harmonic average. The trend is a consequence of the prescribed exponential profile, not experimental confirmation of adsorption-layer thickness.

At fixed film thickness and sliding speed, a higher μeff leads to a larger nominal viscous shear stress τ = μeff u / hr. Therefore, the present calculations cannot establish a stable hydrodynamic lubrication zone, determine hydrodynamic pressure or load-carrying capacity, or demonstrate additive-induced friction reduction. These questions require a couple of Reynolds/contact model and independent experiments. The reported curves are numerical parametric results, not experimental measurements.

5. CONCLUSIONS

A one-dimensional framework has been used to examine how prescribed interfacial viscosity variations affect the equivalent viscosity of a confined lubricant film. The formulation combines a continuous exponential profile with immobile regions of equal thickness at the two boundaries and evaluates the mobile region using harmonic averaging.

Across the three illustrative parameter sets, the calculations show a pronounced increase in effective viscosity as the total film thickness is reduced. The difference between the scenarios is most apparent at the smallest separations and diminishes as the film becomes thicker.

The sensitivity analysis identifies the decay length lh as an important control parameter. A larger value extends the near-interface influence farther into the mobile region and raises the equivalent viscosity. The magnitude of this response depends on the total gap, with thinner films showing the strongest sensitivity.

The numerical values used for the reference oil and interfacial scenarios are prescribed inputs, not experimentally identified properties. The study therefore establishes trends within the adopted model rather than quantitative predictions for a particular commercial lubricant or ZDDP concentration. Further work should combine independent rheological characterization with a pressure- and contact-aware lubrication model, include surface roughness and temperature effects, and test whether the assumed interfacial parameters can be identified from reproducible experiments.

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