Research Article

Effect of Surface Forces on Ultrathin Film Lubrication

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Lubricated contact with nanoscale oil film is modeled for friction. Effect of the van der Waals pressure and the solvation pressure forces on such ultrathin lubricating oil film is considered while finding the friction and other parameters. Hydrodynamic action is represented using transient thermoelastohydrodynamics. Net pressure due to hydrodynamic, solvation, and van der Waals' action is integrated over the contact area to find contact load. Conjunctional friction due to thermal activation of such ultrathin film is derived using the Eyring model. Effect of molecular dimension on friction is studied.

1. Introduction

Ultrathin film transition is in between mixed and boundary regimes of lubrication. In mixed regime of lubrication, the contiguous surface geometry appears in film profile, while in boundary regime a total fluid film rupture occurs and the contiguous solids remain in contact. In between these two lubrication regimes, there exists a transition, where the film is in order of 0.5 nm–5 nm and is termed as ultrathin film. For such a case, the film is of about one or few molecular diameter thicknesses and subjected to solvation and van der Waals' action. Very few attempts were made to know the mechanism of such an ultrathin film and its lubrication performance.

First, Israelachvili [1] has studied the intermolecular surface forces. Henderson and Lozada-Cassou [2] developed a simplified theory to estimate the force between large spheres inside liquid, considering the effect of solvent. They simulated the alignment of the solvent dipoles in vicinity of the sphere and validated the resultant force with experimental finding. Evans and Parry [3] reviewed theoretical and computer simulated studies of atomic-order-fluid film absorbed. They focused on wet phase transition and found that the criticality in a continuously growing wetting film is due to capillary wave like fluctuation, which was best explained. Chan and Horn [4] studied the drainage of thin film between solid surfaces. They measured the transient film thickness, while it is squeezed between two mica surfaces of molecular order smoothness. In this study, film thickness of 0.5 nm

is measured for OMTC (octamethyl-cyclotetrasiloxane), n-hexadecane, and n-tetradecane. For very thin film, the continuum Reynolds equation brakes as the drainage occurs in a series of abrupt steps, whose size matches the thickness of the molecular layer. Trace of water and its dramatic effect on drainage of nonpolar liquid between hydrophilic surfaces cause the film rupture, as they stated.

Matsuoka and Kato [5] postulated ultrathin film lubrication theory to calculate the solvation pressure, for the case of EHL contact. The solvation pressure is calculated by solving the transformed Ornstein-Zernike equation for hard spheres in a two-phase system with Perram's method and using the Derjaguin approximation. They applied this new concept to elastohydrodynamic problems, in which the film thickness is very small and force due to solvation and van der Waals' action is significant. Roelands [6] developed a correlation with viscosity temperature and pressure. Mishra [7, 8] used this correlation to analyze the thermoelastohydrodynamics of a journal-bearing and a piston ring-cylinder liner contact, respectively.

Earlier, Elrod [9] developed a cavitation algorithm that can address the film pressure both in the fluid film and in the cavitation region. It uses a switch function to identify the fluid film and the cavitation region. Swift and Stieber [10, 11] proposed a boundary condition, which works better than the Summerfield and Reynolds boundary condition. Mishra [12] used this boundary condition to study a misaligned elliptic bore journal bearing. Lifshitz [13] developed the

FIGURE 1: Transient nature of lubrication with reduced oil film thickness.

FIGURE 2: Three-dimensional molecular structure of oils.

theory of molecular attractive forces between solids. The limiting case of separation, as compared to wavelength of absorption band of solid, is studied in which the van der Waals force is becoming significant. In this analysis, the effect of temperature is also taken into consideration.

Due to solid-solid contact, the adhesion and stick-slip affect the conjunctural performance [14]. Eyring [15] correlated viscosity, plasticity, and diffusion with an absolute reaction rate. Such a theory yields an equation for the absolute viscosity applicable to cases involving activation energies. The increasing viscosity with shearing stress is explained. Similarly, the same theory yields an equation for the diffusion coefficient, which, when combined with the viscosity and applied to the results of Orr and Butler for the diffusion of heavy into light water, gives a satisfactory and suggestive interpretation. The usual theories for diffusion coefficients and absolute electrical conductance should be replaced by those developed here when ion and solvent molecule are of about the same size. Briscoe and Evans [16] studied shear properties of the Langmuir and Blodgett layers of fluid film. Bowden and Tabor [17] were the first to emphasize the role of relatively moving solids in contact. The role of surface energy in contact of elastic solids is pointed out through the JKR (Johnson, Kendall, and Roberts) model [18]. It improved the earlier Archard's model for elastic deformation and laws of friction.

Based on the literature survey, it is realized that a model of thin film lubrication will be worth presenting with the inclusion of solvation and van der Waals' action (Figure 4).

2. Theory of the Model

When the contiguous surface approaches, just before asperity contact, the van der Waals and solvation pressure forces become active. The mechanism behind the thin film is the molecular level van der Waals force acting in direction opposite to and that of solvation pressure acting in direction of hydrodynamic pressure. The molecular structure of contiguous metal, as well as that of lubricant oil, is important in such circumstances.

2.1. Thin Film Geometry. For many types of conjunctions, the lubrication regime transition occurs. The reason is the approaching or the separation of contiguous solid surface due to nature or magnitude of entraining velocity. The external load that the film bears also plays a significant role. During approaching situation when the film thickness reduced from $0.7\ \mu\text{m}$ to $0.3\ \mu\text{m}$, the roughness of the contiguous solids needs to be addressed, while defining the film thickness for the Reynolds equation (Figure 1). The average flow Reynolds (Patir and Chang) equation is preferred for such a mixed regime.

It leads to the film rupture in the solid-solid contact causing asperity interaction and wear. In between two important transitions, there would be a phase of lubrication, when the film thickness of the lubricant would have the order of two to three molecular diameters. Figures 2(a), 2(b), and 2(c) give the molecular structure of oils commonly used as lubricant. The diameter of the molecules of these oils varies from $1.0\ \text{nm}$,

FIGURE 3: Molecular level ultrathin film contact with different oils.

FIGURE 4: Ultrathin film zone and force balance.

for the case of OMCTS, to 0.25 nm in the case of alkane hydrocarbon and these are nonpolar in nature. For some cases, these are also used as friction protective layer or sealant.

Such molecularly thin film has the tendency of dewetting due to solvation that reduces the localized friction near the asperity tip. Figure 3 represents the relatively placed oils and the solid layer in contact where the solvation effect

is dominating. Sometimes, due to dewetting, the metallic surface behaves as the smooth surface to minimize the severity of the asperity interaction.

2.2. Solvation. Solvation has a dominant effect. Such an ultrathin film, as discussed earlier, possesses the dewetting action of solvation that prevents the formation of meniscus

and reduces the chance of adhesion. The solvation is more effective in the case of a lubricant with smaller size molecules (<2.0 nm). Lubricant with longer chain molecules has negligible effect of solvation. The solvation pressure (as given in (1)) is a function of the contact density parameter and the film ratio (h/d_m), with d_m being diameter of the lubricant molecule. The contact density is the bulk density of the fluid, which is the function of change in density (difference in the density of film in conjunction with that of film in a single free surface) and the Stephen Boltzmann's constant and the temperature of oil, as given as follows:

$$P_s = -Ce^{-h/d_m} \cos\left(2\pi \frac{h}{d_m}\right), \quad (1)$$

where

$$C = K_b T \rho (h \rightarrow \infty),$$

$\rho (h \rightarrow \infty) \rightarrow$ corresponding value for single surface,

$$h \geq d_m. \quad (2)$$

T is temperature rise in oil due to friction.

The film ratio is defined as the ratio of the film thickness to the molecular diameter of the lubricant oil. For any type of lubricant conjunction, the rise in temperature occurs due to the rapid shear of lubricant layer. The solvation effect dominates the gap, which is of several molecular diameters. It happens due to the density variation of liquid near the solid boundary. The dewetting action of solvation guards against formation of meniscus and prevents adhesion. The solvation is more pronounced for small fluid molecules such as perfluoropolyether and OMCTS/octamethyl-cyclotetrasiloxane, which are nominally spherical molecules (1–1.5 nm). Such an effect is negligible for long chain molecules. Table 1 represents the molecular specification of different oils.

2.3. Van der Waals' Pressure. The van der Waals force is a weak attractive force, which is mainly responsible for binding the organic molecule of the lubricant to asperity in the contiguous metal surface. It is given in the following equation:

$$F_w = \sum P_w dA, \quad (3)$$

where

$$P_w = -\frac{A_h}{6\pi h^3}, \quad (4)$$

$A_h \rightarrow$ the Hamaker constant

or

$$A_h = \pi^2 C_a \rho_m \rho_l, \quad (5)$$

where

$$C_a = -r^6 \omega(r),$$

A_h lies in between $(10^{-21} - 10^{-19} J)$ (6)

$$A_h = 1.4 \times 10^{-20} J.$$

In this case ρ_m and ρ_l are number of atoms per unit volume in the surfaces of metal and lubricant. C_a is the coefficient in particle pair interaction and is found in van der Waals' interaction. The van der Waals force is effective only for few hundred angstroms.

2.4. The Casimir-Polder Pressure. In lubricated contact, there is the attraction force between to contiguous solids beyond the van der Waals limit up to few micrometers. Such pressure is given as

$$\frac{F_c}{A} = P_{\text{cas}} = \frac{\hbar c \pi^2}{240 h^4}, \quad (7)$$

where F_c is the Casimir force, P_{cas} is the pressure due to the Casimir force, h is reduced Planck's constant, and c is the speed of light.

2.5. Conjunction Friction due to the Eyring Shear. Ultrathin film adsorbed in molecularly thin and smooth surface is subjected to shearing due to thermal activation (see (8)) based chemical reactions. It is non-Newtonian in nature. The potential barrier in thermal activation is given in the following equation. In this circumstance, the Eyring model can better describe contact conjunction fluid viscosity. Johnson [14] expressed the Eyring shear stress (see (9)) as function of velocity, pressure, and temperature. Consider the following:

$$E_y = Q - p\Omega - \tau\phi, \quad (8)$$

if $\frac{\tau\phi}{K_b T} > 1.$

Potential barrier in thermal activation is given as

$$\tau = \tau_y + \xi\rho, \quad \left(\because \xi = \frac{\Omega}{\phi}\right). \quad (9)$$

The Eyring shear stress is determined as

$$\tau_y = \frac{1}{\phi} \left[K_b T \ln \left(\frac{U}{v_f} \right) + Q \right], \quad (10)$$

where v_f is characteristic velocity related to frequency process. Therefore,

$$\tau_y = \frac{K_b T}{\phi} \ln U + \tau_{yr} - \rho P_v, \quad (11)$$

$$\tau_{yr} = \frac{1}{\phi} [Q - P_v \Omega + K_b T \ln v_f]. \quad (12)$$

In (12), the following substitution is made as follows:

$$\frac{K_b T}{\phi} \approx \frac{3.4}{A}, \quad \tau_{yr} \approx \frac{11.3}{A}, \quad \xi = 0.16 \quad (13)$$

$$F = \iint \tau_y dx dy, \quad \tau_y > 0.$$

TABLE 1: Molecular specification of several oils.

Lubricant type	Compound name	Chemical formula	"C" value in MPa	Molecular diameter (nm)	Density (gm/mL)	Molecular structure
A	OMCTS/silicon oil	$[\text{Si}(\text{CH}_3)_2\text{O}]_4$	172 MPa	1.0 nm	0.956
B	Hexadecane/cetane	$(\text{C}_{16}\text{H}_{34})$	62 MPa	0.4 nm	0.77
C	Tetradecane/alkane hydrocarbon	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	49 MPa	0.25 nm	0.756

2.6. *The Reynolds Equation.* The Reynolds equation is a second-order differential equation which correlates the hydrodynamic pressure with film, entraining velocity, and lubricant viscosity and density. The Reynolds equation in this case is given as

$$\frac{\partial}{\partial x} \left(\frac{\rho h^3}{\eta} \frac{\partial P_h}{\partial x} \right) + \frac{\partial}{\partial y} \left(\frac{\rho h^3}{\eta} \frac{\partial P_h}{\partial y} \right) = 12 \left\{ U \frac{\partial P_h}{\partial x} + V \frac{\partial P_h}{\partial y} + \frac{\partial}{\partial t} (\rho h) \right\}. \quad (14)$$

It is for the full fluid film region. The hydrodynamic pressure for both fluid film and cavitation region is given as

$$P_h = g\beta \ln \theta + P_c, \quad (15)$$

where

$$g = \begin{cases} 1 & \rightarrow \text{for full film,} & \text{if } \theta \geq 1 \\ 0 & \rightarrow \text{for cavitation region,} & \text{if } \theta \geq 0. \end{cases} \quad (16)$$

θ is the fractional film content and g is the switch function. The Reynolds equation with cavitation inclusion turned to

$$\frac{\partial}{\partial x} \left(\frac{\rho_c h^3}{\eta} g\beta \frac{\partial \theta}{\partial x} \right) + \frac{\partial}{\partial y} \left(\frac{\rho_c h^3}{\eta} g\beta \frac{\partial \theta}{\partial y} \right) = 12 \left\{ U \frac{\partial \rho_c h}{\partial x} + V \frac{\partial \rho_c h}{\partial y} + \frac{\partial}{\partial t} (\theta \rho_c h) \right\}. \quad (17)$$

The Couette flow in the cavitation region leads to

$$\left(U \frac{\partial}{\partial x} + V \frac{\partial}{\partial y} + \frac{\partial}{\partial t} \right) (\theta \rho_c h) = 0. \quad (18)$$

The Dowson and Higginson equation for density variation is

$$\rho = \rho_0 \left(1 + \frac{0.6 \times 10^{-9} \times P_h}{1 + 1.7 \times 10^{-9} \times P_h} \right). \quad (19)$$

The viscosity variation is based on combined law as follows:

$$\eta = \eta_0 e^{\alpha P_h}, \quad (20)$$

where

$$\alpha = (\ln \eta_0 + 9.67) \frac{\left[\left\{ 1 + P_h / 1.98 \times 10^8 \right\}^z - 1 \right]}{P_h}, \quad (21)$$

$$Z = \frac{\alpha_0}{\{5.1 \times 10^{-9} (\ln \eta_0 + 9.67)\}}.$$

Total conjunctural pressure at any instant of time is given as

$$P_T = P_h + P_w + P_s, \quad (22)$$

where P_T is the total lubrication pressure, P_w is the van der Waals pressure, and P_s is pressure due to solvation. Therefore the load bearing ability is

$$W = \int P_T dA. \quad (23)$$

2.7. *Solution Steps.* The van der Waals force and the solvation pressure force are active for film of nanometer thickness. In this analysis, we have taken the film of 2.0–3.0 nm (which is equivalent to three layers of oil molecule). For a film profile of this order, the solvation pressure and the van der Waals pressure are calculated as per (1) and (3). Corresponding hydrodynamic pressure is calculated by solving the Reynolds

FIGURE 5: (a) Film profile-A. (b) Solvation pressure (due to film-A). (c) Van der Waals' pressure (due to film-A).

FIGURE 6: (a) Film profile-B. (b) Solvation pressure (due to film-B). (c) Van der Waals' pressure (due to film-B).

FIGURE 7: Solvation pressure due to nanoscale oil film of (a) OMCT, (b) hexadecane, and (c) tetradecane.

FIGURE 8: Van der Waals' pressure due to nanoscale oil film of (a) OMCT, (b) hexadecane, and (c) tetradecane.

FIGURE 9: Friction for different contact due to the Eyring condition.

FIGURE 10: The maximum Eyring stress variation due to entraining velocity.

equation. Load convergence and film relaxation are not required as the estimation is based on exact film. Further, the Eyring stress and corresponding friction are calculated as per (11). When there is further squeezing action, the film fails and the contact situation changes drastically. There occurs the asperity contact and boundary friction for which the wear of contiguous solid occurs.

3. Result Analysis

Figure 5(a) shows a parabolic film profile with 2.5 nm thickness. The corresponding solvation pressure and the van der Waals pressure are given in Figures 5(b) and 5(c), respectively. Such profile matches with the slider pairs like ring liner. Similarly, Figure 6(a) shows a profile, which is parabolic in entraining direction with a globally deformed profile along the side leakage direction. The corresponding solvation pressure and the van der Waals pressure are plotted (Figure 8).

FIGURE 11: Surface force beyond van der Waals' boundary up to 25 nm.

There is a change in the solvation and the van der Waals pressure profile due to film profile modification out of local and global deformations. Figure 7 shows the 3D profile of solvation pressure due to ultrathin film of OMCTS, hexadecane, and tetradecane, respectively. It predicts that different oil molecule has different molecular structure thereby different solvation pressure profile.

Figure 9 shows the van der Waals pressure profile for all the three types of oils (OMCTS, hexadecane, and tetradecane). The van der Waals pressure is independent of oil molecular arrangement. Figure 9 shows the friction due to the Eyring stress. The oil with smaller molecular diameter has less friction due to the Eyring condition. Again, the point contact causes more friction than semiconformal or conformal contact.

With increasing velocity, the Eyring stress increases (Figure 10). It is more in the case of long chain molecules. Figure 11 shows the Casimir-Polder pressure.

4. Conclusion

Nanoscale film exists and performs prior to the film rupture in almost all types of lubricated contacts. Combined action of the solvation and the van der Waals action remains dominant and governs the lubrication performance in this case. The net pressure is the vector sum of these two pressures along with hydrodynamic pressure. Such consideration has more detail of molecular and nanoscale ultrathin film performance for both mechanical and biological contacts.

Nomenclature

- A_h : Hamaker's constant (J)
- C : Solvation pressure constant (m)
- C_a : Coefficient of particle pair interaction (m)
- c_l : Speed of light (ms^{-1})
- d_m : Molecular diameter (m)

E_y : Barrier height for Eyring
 F : Friction force (N)
 F_c : Casimir's force (N)
 F_w : Van der Waals' force (N)
 g : Switch function
 h : Film thickness (μm)
 $\hbar$: Reduced Planck's constant
 K_b : Boltzmann's constant (J K^{-1})
 p_h : Hydrodynamic pressure (Mpa)
 P_s : Solvation pressure (Mpa)
 P_w : Van der Waals' pressure (Mpa)
 Q : Process activation energy (J)
 r : Contact curvature radius (m)
 T : Temperature of the lubricant ($^{\circ}\text{C}$)
 U : Velocity in direction of entrainment (ms^{-1})
 V : Velocity in side leakage direction (ms^{-1})
 v_f : Characteristic velocity related to frequency (ms^{-1})
 x : Coordinate in entraining direction
 y : Coordinate in side leakage direction
 W : Load bearing ability (N)
 Z : Pressure viscosity index
 θ : Fractional film content
 β : Lubricant bulk modulus
 ρ : Lubricant density
 ρ_l : Number of atoms per unit volume in surface of lubricant
 ρ_m : Number of atoms per unit volume in surface of metal
 τ : Shear stress (Mpa)
 τ_y : Pressure dependent shear stress (Mpa)
 τ_{yr} : Velocity dependent shear stress (Mpa)
 ξ : The Eyring model constant
 ϕ : Activation volume (m^3)
 η : Lubricant dynamic viscosity
 α : Pressure viscosity coefficient (Pa^{-1}).

Conflict of Interests

The author declares that they have no conflict of interests regarding the publication of this paper.

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