

Particle Entrainment in Lubricants Leads to Extended Mixed Lubrication in Soft Tribology

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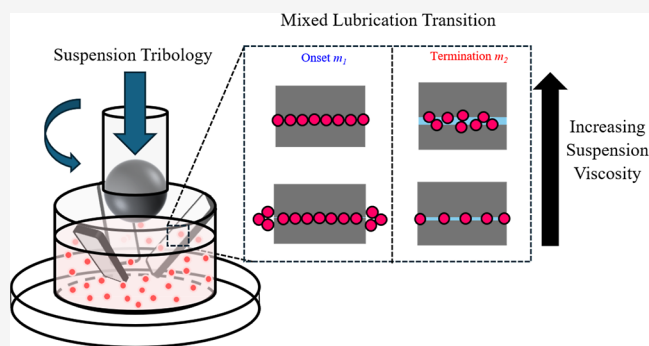
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ABSTRACT: Particle-laden lubricants provide a versatile platform for tuning frictional behavior across boundary, mixed, and elastohydrodynamic (EHL) regimes in soft tribological systems. In this study, we examine the evolution of an extended mixed regime between poly(dimethylsiloxane) (PDMS) tribopairs lubricated with poly(methyl methacrylate) (PMMA) suspensions in low-viscosity squalene and high-viscosity diisodecyl phthalate (DIDP). Smaller particles at low concentrations delay entrainment and slow film formation, while larger particles consistently reduce friction by enhancing load distribution and promoting separation that limits solid–solid contact. These effects, driven by particle confinement and structural rearrangements, generate clear deviations from classical Stribeck behavior. Two characteristic points mark the onset and termination of this extended mixed regime. We observe that the velocity corresponding to the beginning of mixed regime transition, U_{m1} , is largely independent of particle size and volume fraction in squalene suspensions due to a restrictive particle confinement within the tribopairs that primarily allows solvent movement through the gap. In contrast, DIDP suspensions have a lower onset velocity (U_{m1}) as the higher solvent viscosity promotes particle entrainment into the lubrication gap. The velocity corresponding to the end of the mixed regime transition (U_{m2}) decreases with increasing volume fraction, indicating the formation of a fully developed lubrication film that separates the PDMS tribopairs. Hamrock–Dowson film thickness estimates combined with experimental relaxation measurements are used to quantify the development of the lubrication film as sliding speed increases and the system approaches the EHL regime. The findings from this study establish particle entrainment and suspension viscosity as key mechanisms for expanding and stabilizing the extended mixed regime.



INTRODUCTION

In biology and in engineered materials, friction modulation between two sliding surfaces is commonly accomplished by separating the solid surfaces that would otherwise come into adhesive solid–solid contact. Physicochemical strategies such as reducing the surface roughness, grafting or adsorption of molecular additives, or incorporating interfacial lubricants have proven effective in reducing both adhesive and viscous dissipation.^{1–4} In cases where the two sliding surfaces, so-called tribopairs, are compliant and deform dynamically during compression and sliding, liquid lubricants containing nano- and microparticles have emerged as particularly promising systems for tailoring the interfacial friction.^{5–7} This is because particles can undergo microstructural rearrangements and may bear load more effectively than solvent molecules, particularly within the boundary friction regime by acting as “ball bearings” or sliding platelets, and also within the mixed regime of lubrication where the lubricant just begins to lift the surfaces

away from each other. There are also examples of particles that add resistance to sliding, often in situations where contaminants or debris work their way into the sliding contact and cause irreversible wear of the surfaces. For instance, silica microspheres,⁸ pure carbon microspheres,⁹ graphene balls,¹⁰ fullerene-like nanoparticles¹¹ and poly(*N*-isopropylacrylamide) grafted carbon microspheres have been used to produce rolling friction at the contacting surfaces.¹² Although these particles are added as friction modifiers, they do not necessarily cause a reduction in the measured friction because aggregation of

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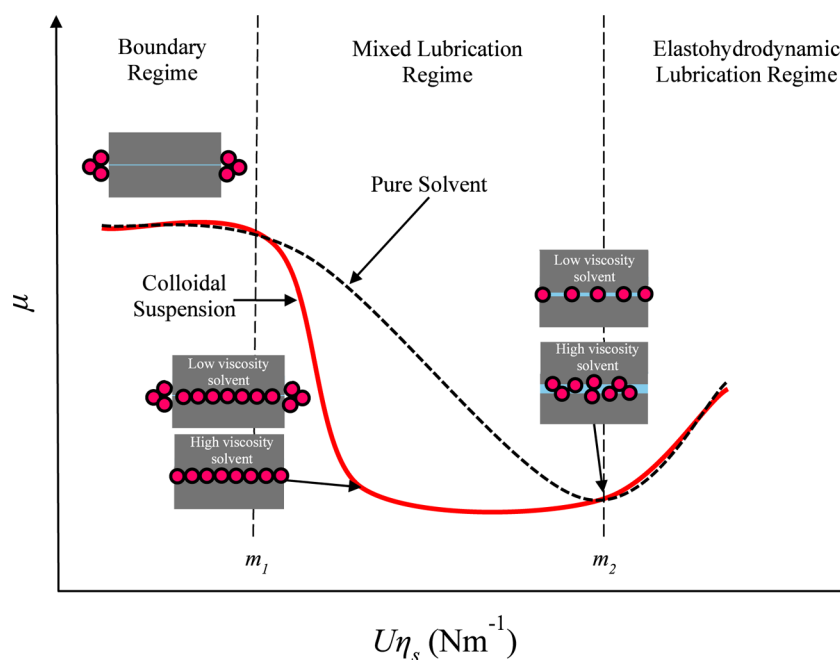


Figure 1. Sketch of the Stribeck curve where the steady sliding friction coefficient (μ) is plotted against the product of sliding speed (U) and lubricant viscosity (η_s). Mixed regime for systems with pure solvents (black dotted line) is much sharper than that for systems where the particulate suspension acts as the lubricant (solid red line). The flat or extended portion of the mixed regime is attributed to the entrainment of particles within the contact. Entrainment is driven by the different combined interaction between the tribopair surface, suspension properties, and the nature of the particles.¹⁸

particles as well as the surface energy of the counter surfaces plays a role in the resulting friction mechanism.^{13,14} Studies of compliant lubrication systems reveal that friction depends strongly on the particle-to-gap size ratio, reflecting the coupled effects of substrate deformation, hydrodynamic lift generation, and confinement in determining whether particles provide beneficial load support or increase wear.^{8,15–17} Most tribological studies of particle-laden lubricants are conducted with highly compliant (elastic moduli ~ 0.1 kPa – 150 kPa) particles^{18,19} which tend to increase wear on the surface. However, there are instances of soft lipid particles which are sheared to create a lubrication layer.¹⁷ How particle lubricants should be designed to protect against the solid–solid contact of tribopairs across a wide range of sliding conditions is less clear, especially when deformable tribopairs are used.

The Stribeck curve describes three lubrication regimes that exist in tribological contacts: boundary, mixed lubrication (ML) and elastohydrodynamic lubrication (EHL).²⁰ A minimum in the friction coefficient is typically observed at the transition between the mixed and the EHL regime. Extending this low friction transition region across a broader range of sliding speeds and lubricant viscosities is often important for improving the tribological performance in a variety of synthetic and biological systems. One of the reasons for the extension of the ML regime beyond the standard Stribeck behavior is illustrated in Figure 1. Here we show a classical Stribeck curve depicting the three main friction regimes, for a fully flooded contact where a molecular lubricant is present. The Stribeck curve plots the friction coefficient, $\mu = F_S/F_N$, where F_N is the normal force and F_S is the shear force, as a function of the dimensionless Sommerfeld number $S = UhL/F_N$, where U is the tribopair relative sliding velocity, L is the length of the contact line, and h is the lubricant viscosity. Variants of this definition of S exist, for example by replacing

the L term with dimensions for patterned surfaces²¹ or by having a normalized velocity V which includes the substrate shear modulus G and indenter radius R ($V = U\eta R^{5/3}G^{1/3}F_N^{-4/3}$),²² but the overall message is the same: the Stribeck curve tracks m as the two tribopairs undergo steady compressive sliding. At a given F_N and low U associated with the boundary friction regime, the tribopairs are pressed against each other, separated only by molecularly thin layers of fluid or surface additives. If particles that roll or slide easily are present within the highly confined gap, EHL transitions tend to occur at lower U because the tribopairs are deformed by the fluid pressure and separated from each other due to a pressure gradient and corresponding lift force.^{23,24} The viscosity of particle-laden lubricants can be treated as a continuum approximation by using an effective bulk suspension viscosity within the EHL regime because the gap is often much larger than the particle dimensions.

An interesting mixed regime sits between boundary and EHL friction in which m is at its lowest point. Here, with increasing velocity, the solid surfaces are just beginning to separate, and larger lubricant particles or molecules may become entrained partially in the small gap. The mixed regime is denoted by the collection of dynamic conditions under which the contact region is partially wetted by the lubricant. Therefore, the overall friction results from combined effects of fluid film lubrication and solid asperity contact. When the mixed regime is approached from the EHL regime by a decrease in U , the gap height becomes small compared to asperity height, and mechanical instabilities when transitioning from full-film lubrication to Schallamach waves,^{25,26} and to stick–slip motion^{27,28} caused by attractive interactions occur near the interface.²⁹ On the other hand, squeeze flow of the lubricant controlled by interfacial wettability and the amount of fluid in the confined gap becomes the driving force at the

boundary to mixed transition regime.²⁹ The gap height is controlled by the balance between hydrodynamic lift and elastic deformation of the contacting substrates, resulting in a confined lubrication layer in which the fluid, entrained particles, and deformable surfaces collectively support the load and contribute to frictional dissipation.¹⁸ This suggests that the mixed regime transitions from the boundary- or EHL-side depend on the relative size of the particles to the evolving gap thickness, as well as the balance between elastic deformation, particle mobility, and confinement within the contact.

If the goal were to achieve low friction, it would certainly be most efficient for the system to remain as close as possible to the ML regime. In reality, the extreme conditions and variability that machined parts and gears must endure, combined with the hard materials that comprise these tribopairs, mean that tribopairs are operated at higher operating velocities to avoid crossing into the boundary regime where solid contact could mean catastrophic wear. Interestingly, biological systems such as articular cartilage can extend the mixed regime across a broader range of sliding speeds,^{30,31} where an elastoviscous transition (essentially an extended mixed regime like the type shown in Figure 1 instead of full hydrodynamic lubrication) was observed despite the presence of pressurized lubricants between the surfaces.^{30,32} These studies also showed that a high concentration of hyaluronic acid at the interface shifts the elastoviscous transition toward lower friction and a regime consistent with low-friction viscous boundary lubrication. This elastoviscous transition, similar to the extension of the ML regime in this study, has been attributed to the formation of a concentrated, structured interfacial layer that enhances load support and maintains surface separation. Therefore, aggregation of colloid-sized macromolecules or particles at soft polymeric interfaces could help reduce interfacial friction. Another example of particle-laden suspensions extending the mixed regime was also demonstrated with glass beads between soft tribopairs¹⁸ and in our current work.

In this study, we investigate the effect of size and volume fraction of particle-laden lubricants on the mixed lubrication regime between compliant substrates made out of poly(dimethylsiloxane) (PDMS). Colloidal poly(methyl methacrylate) (PMMA) particles with sizes ranging from 0.43–3.1 μm are suspended in two solvents of different viscosities, squalene (0.012 Pa·s) and diisodecyl phthalate (DIDP) (0.10 Pa·s). The suspensions are prepared at a range of concentrations ranging from dilute to highly concentrated volume fractions ($\phi = 0.01$ –0.55). Once prepared, the tribopairs are sheared at fixed normal loads and a range of velocities ($8 \times 10^{-5} \text{ m/s} \leq U \leq 8.3 \text{ m/s}$) to span the boundary to EHL regimes. We find that particle-laden lubricants generate two critical points in the Stribeck curves, m_1 and m_2 , that mark the boundaries of the extended mixed regime between the boundary and EHL regimes; these points indicate how the load is being carried by the solvent and the particles. We also leverage a sliding indenter setup and the Hamrock–Dowson equation to estimate the central lubrication film thickness in these extended mixed regimes for these tribopairs. The results suggest that the viscous properties of the solvent in the suspension are responsible for the extended mixed lubrication regime. Specifically, the beginning of this regime (m_1) is marked by the breakdown of the continuum approximation for particles but not for the solvent because the gap is very small

($h \approx 40 \text{ nm}$). This effect is apparent for squalene, which has a lower viscosity than DIDP. Particles become entrained on the PDMS when squalene is the solvent while DIDP's higher viscosity generates a larger gap and allows for a less restricted flow of both particles and solvent into the contact zone. A full lubrication film begins to develop at the end of the mixed regime (m_2) where the velocity of the transition decreases with an increase in the particle volume fraction. Figure 1 shows a sketch of the mechanisms responsible for these transition points. These mechanisms are quantified to show the solvent dependent effect on μ and transition U in the context of particle exclusion and entrainment. Furthermore, we investigate post sliding relaxation dynamics to confirm the influence of particle size on film formation.

MATERIALS AND METHODS

Materials

Sylgard 184 elastomeric PDMS kit containing a PDMS polymer base and a curing agent was purchased from Dow Corning. All other chemicals used in this study were procured from Sigma-Aldrich. Methacrylic acid (MA, 99.0%), 1-octanethiol ($\geq 98.5\%$), hexane ($\geq 97.0\%$), dodecane ($\geq 99.0\%$), squalene ($\geq 98.0\%$) and diisodecyl phthalate ($\geq 99.0\%$) were used without further purification. Methyl methacrylate (MMA, 99.0%) was treated with a prepacked column to remove the inhibitors hydroxyquinone and monomethyl ether hydroxyquinone. Azo-bis-isobutyronitrile (AIBN) was recrystallized in acetone and stored in a refrigerator at 4 °C. The poly(12-hydroxystearic acid)-(glycidyl methacrylate)-(methyl methacrylate) (PHSA-GMA-MMA) block copolymer was prepared in the lab based on the protocol described by Pradeep et al.³³

Synthesis of PDMS Tribopairs

Sylgard 184 base and its curing agent were mixed in a 10:1 (wt/wt %) ratio. The resulting mixtures were blended with a planetary centrifugal mixer (AR-250 Thinky) using a 30 s period for both mixing and defoaming cycles. Samples were poured into glass molds and placed in vacuum (60 kPa) for 45 min to remove any trapped air bubbles. The polymer mixture was cured at 80 °C for 2 h in an oven. Rectangular slabs measuring 0.6 cm $\times$ 1.5 cm were cut for tribological analysis. Spherical PDMS balls with a diameter of 12.7 mm were also produced for tribology using an identical mixing and curing process within a specialized stainless-steel mold. The root-mean-square (S_q) roughness for the pristine PDMS slabs and balls was measured by optical profilometry using laser scanning microscopy (Keyence VKX1100) with a 20X dry objective. The value of S_q was found to be $0.09 \pm 0.02 \mu\text{m}$.

Synthesis of PHSA–PMMA Colloidal Particles

Poly(methyl methacrylate) (PMMA) colloidal particles were synthesized using a free-radical dispersion polymerization technique as described elsewhere.³³ Briefly, a solution of 7.5 g of hexane and 2.5 g of dodecane was uniformly mixed with 1.2 g of PHSA in a round-bottom flask at 80 °C. Then, a mixture of 10.0 g MMA, 200 μL MA, and 75 μL 1-octanethiol was added to the flask. The polymerization was initiated by adding 8.5 mg AIBN. The nucleation and oligomer formation began within 4–6 min as indicated by the onset of turbidity in the solution. The reaction was allowed to proceed for 2 h. To enable visualization using confocal laser scanning microscopy (CLSM), 3 mg of Nile red dye was added in the second step. Once the reaction was completed, the particles were cleaned by centrifuging them six times with hexane at 1000 g-force for 10 min. The cleaned particles were stored dry in amber bottles until further use.

Preparation of Colloidal Suspensions

Colloidal suspensions were prepared by suspending the sterically stabilized particles in squalene and DIDP. The particles were charge neutral and refractive index-matched with the solvent to ensure

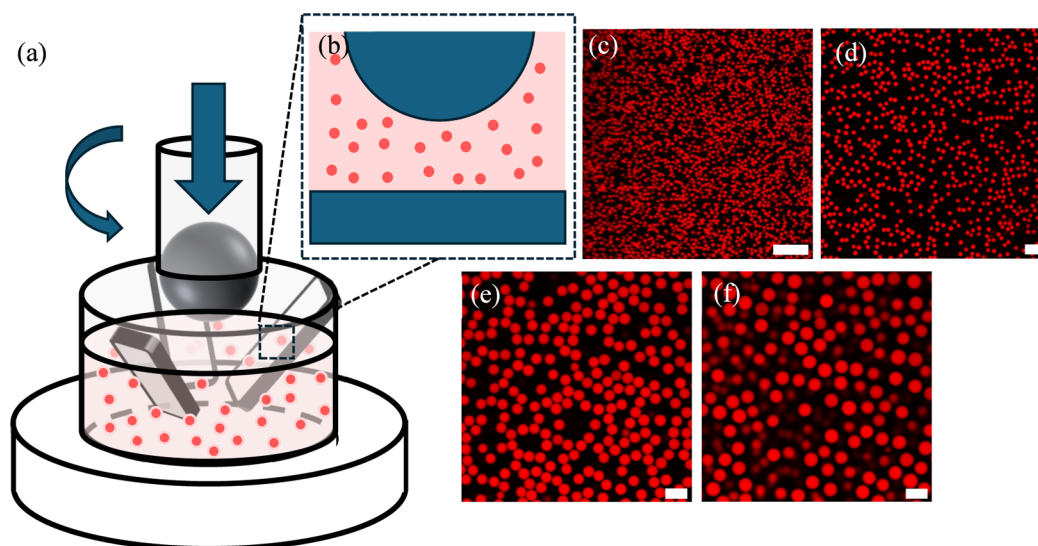


Figure 2. (A) Sketch of a ball-on-3-plates tribology setup to determine the Stribeck behavior of particle suspensions sheared between soft tribopairs. (b) Schematic of the contact region containing Poly(methyl methacrylate) (PMMA) suspensions between PDMS–PDMS tribopairs. Representative confocal images of PMMA colloidal particles prepared with different particle diameters: (c) $2a = 0.43 \mu\text{m} \pm 3\%$ (d) $2a = 1.0 \mu\text{m} \pm 3\%$, (e) $2a = 2.5 \mu\text{m} \pm 5\%$, and (f) $2a = 3.1 \mu\text{m} \pm 3\%$. All scale bars are $5.0 \mu\text{m}$.

suppression of electrostatic and van der Waals forces. In an earlier paper, we show that these suspensions exhibit hard-sphere-like properties.³³ The suspensions at different volume fractions (ϕ) were prepared by first centrifuging the suspension at gravitational Peclet number, $Pe_g = (4\pi\Delta\rho g a_{\text{eff}}^4)/3k_B T = 1000$ to generate dense sediments at jamming fraction, $\phi_j = 0.64 \pm 0.01$ where $\Delta\rho$ is the density mismatch between the solvent and the particles, k_B is the Boltzmann constant, and T is the temperature. The value of ϕ_j for smooth colloids is in agreement with simulations that account for size polydispersity.^{34–36} The jammed sediments were then diluted to desired ϕ by adding the appropriate amount of squalene (dynamic viscosity = $0.012 \text{ Pa}\cdot\text{s}$) and DIDP (dynamic viscosity = $0.10 \text{ Pa}\cdot\text{s}$). The suspensions were left on horizontal rollers for 5 days to redisperse, and a homogeneous suspension was formed. The value of ϕ is independently verified using CLSM (Figure 2c–f). Particle centroids were counted (N_p) within 3D image volumes of the suspensions, V_{box} , and particle volume fraction was estimated with $\phi = \frac{4\pi a^3 N_p}{3V_{\text{box}}}$, where a is the particle radius. The particle diameter ($2a$) was estimated based on the 2D confocal microscopy images of colloidal suspensions near the coverslip, where particles form a monolayer. This measurement of the particle diameters accounted for swelling of PMMA particles in the solvents. The particle diameters were obtained based on at least 50 particles to minimize statistical uncertainty. We use particles of four different sizes with $2a = 0.43 \mu\text{m} \pm 3\%$, $1.0 \mu\text{m} \pm 3\%$, $2.5 \mu\text{m} \pm 5\%$, $3.1 \mu\text{m} \pm 3\%$.

Rheology

Steady shear rheology experiments were conducted on a stress-controlled rheometer (TA Instruments, DHR-2) using a 50 mm parallel plate geometry at room temperature, 20°C . The top and bottom plates were roughened by adhering 1500 grit sandpaper (roughness $R_a = 1.8 \pm 0.5 \mu\text{m}$) to minimize wall slip. The viscosity (η) of the colloidal suspensions was measured by performing steady flow sweeps in which the applied stress (σ) was progressively increased from 0.01 to 100 Pa. At each point, the shear rate ($\dot{\gamma}$) was measured and averaged over a period of 120 s. All experiments were performed at a fixed gap height of $500 \mu\text{m}$ to avoid confinement effects.

Tribology

A ball-on-three-plate geometry attached to a stress-controlled rheometer (DHR-2, TA Instruments) at a constant temperature of 20°C was used to measure the Stribeck behavior of the tribopairs.

The setup consisted of a PDMS ball of diameter 12.7 mm attached to the upper geometry while the bottom section had three PDMS slabs of dimension $20 \times 10 \times 2 \text{ mm}$ inserted. A fixed axial force of 1.5 N was applied to the tribopairs for suspensions prepared in squalene and DIDP. The viscosities of the suspensions varied with particle volume fractions and solvent viscosities. Steady sliding tests were performed with an upward velocity sweep from 0.001 to 100 rad s^{-1} for a total of 43 min. An equilibration time of 90 s was maintained at each data point to allow the system to attain steady state. After each experiment, fresh PDMS tribopairs were used to ensure that no wear tracks from previous tests were present. All data points shown are from 3 independent replicates with both the PDMS tribopairs and lubricating suspension being replaced between experiments.

Film Relaxation Dynamics from Shear Cessation

A previously reported³⁷ slide-and-stop method to measure the film thickness during sliding was adapted for use in our experiments. Initially, PDMS substrates coated with a thin film of DIDP particle suspensions as the lubricant were placed on a glass slide which was mounted on a rigid metal plate. A PDMS indenter was lowered into contact with the lubricated substrate and slid laterally across its surface at a specified speed under fixed vertical load while the vertical displacement of the indenter was recorded continuously. Sliding was conducted over a distance of 12 mm, after which the motion was stopped abruptly to initiate a relaxation phase. Throughout both sliding and relaxation, the applied normal load was held constant by moving the indenter vertically under a proportional-integral-derivative (PID) feedback control loop system. At the end of the sliding stage, the system relaxes (the film thickness decreases) as the applied normal load drives liquid out of the contact region. Just before the end of the sliding phase, the vertical position of the indenter was recorded as h_1 . After the subsequent relaxation, it was recorded as h_2 . The change in distance was $\Delta h = h_1 - h_2$. This displacement reflects contributions from the lubricant film thickness and the substrate's deformation. To exclude the influence of the substrate deformation and extract the film thickness for the DIDP system, the glycerol lubricant system was used as a reference. Under these experimental conditions, the film thickness for the glycerol was negligible compared with the DIDP case. Thus, the film thickness for DIDP systems $h_{\text{DIDP}} = \Delta h_{\text{DIDP}} - \Delta h_{\text{glycerol}}$. The corrected heights are then denoted as h_0 at the moment when the indenter stops sliding and h_f after relaxation. At $U = 2.0 \times 10^{-4} \text{ m/s}$, a normal force of 152, 120, and 169 mN was applied when using DIDP suspensions of $2a = 1.0 \mu\text{m}$, $2a = 2.5 \mu\text{m}$,

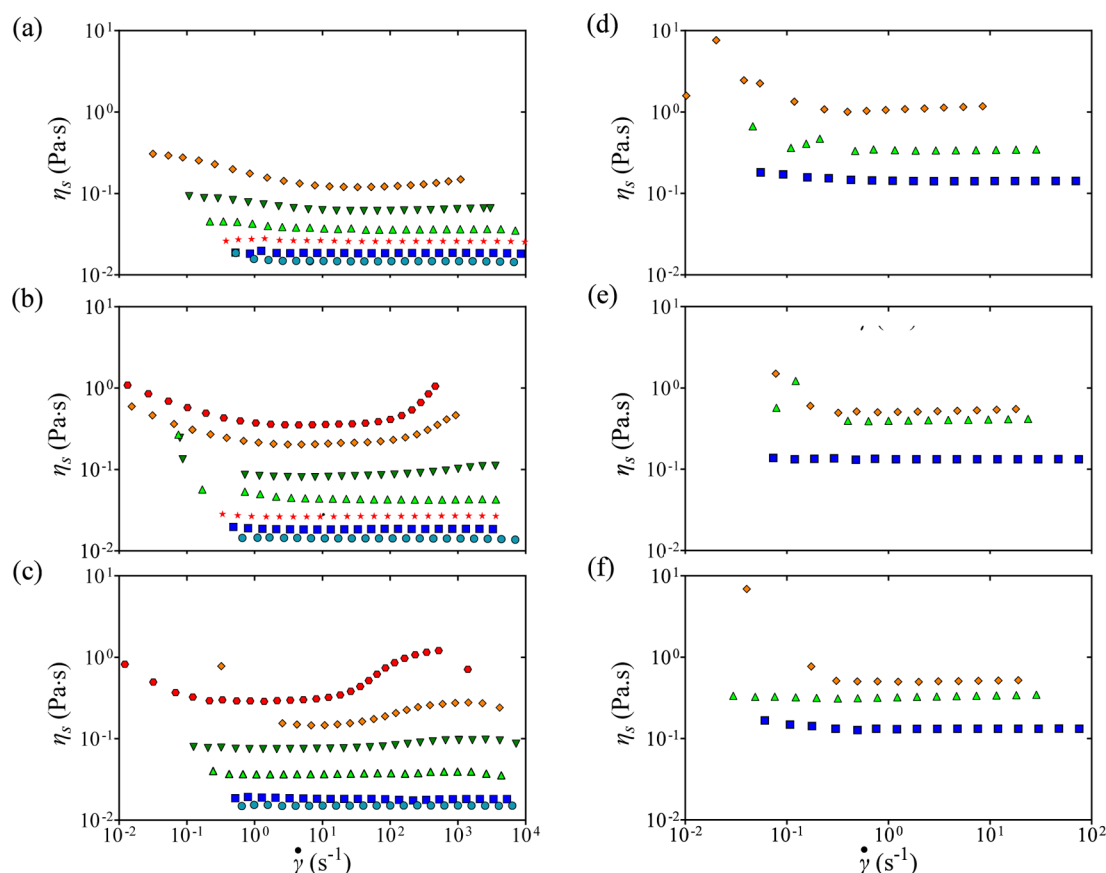


Figure 3. Steady shear viscosity (η_s) measurements as a function of applied shear rate ($\dot{\gamma}$) on PMMA colloidal suspensions prepared in (a–c) squalene and (d–f) diisodecyl phthalate (DIDP). Particle diameters are (a) $2a = 0.43 \mu\text{m}$, (b) $2a = 1.0 \mu\text{m}$, (c) $2a = 2.5 \mu\text{m}$, (d) $2a = 1.0 \mu\text{m}$, (e) $2a = 2.5 \mu\text{m}$, and (f) $2a = 3.1 \mu\text{m}$. Different volume fractions of the suspensions include $\phi = 0.01$ (cyan filled circle, $\circ$), $\phi = 0.1$ (blue filled square, $\square$), $\phi = 0.2$ (solid red star, $\star$), $\phi = 0.3$ (light green upward triangle, $\triangle$), $\phi = 0.4$ (dark green downward triangle, ∇), $\phi = 0.5$ (orange diamond, $\diamond$), and $\phi = 0.55$ (red hexagon, $\hexagon$).

and $2a = 3.1 \mu\text{m}$ respectively. $\phi = 0.5$ was kept constant for all particle diameters.

RESULTS AND DISCUSSION

Suspension Viscosity

Suspensions of different viscosities and particle sizes allow investigation of the competing forces of hydrodynamic lubrication and particle confinement in soft lubricated contacts. From Reynolds lubrication theory, we know that the suspension viscosity directly governs the magnitude of hydrodynamic pressure generation which could determine whether a particle is entrained or excluded from the contact zone. Lubrication film thickness also scales with viscosity, so tuning the suspension viscosity with particle size and volume fraction affects how the fluid pressure and particle confinement affect friction. Therefore, we can determine if the mechanism behind the observed friction behavior is due to interparticle interactions, solvent flow, or a combination of both.

Figure 3 shows that the viscosity (η_s) of colloidal suspensions prepared in both squalene and DIDP at different shear rates ($\dot{\gamma}$) increased with increasing volume fraction (ϕ) across all particle sizes tested. Steady state viscosity readings were taken from the plateau region just before the thickening commences. The relative viscosity ($\eta_{r,s} = \eta_s/\eta_0$) was evaluated and plotted against ϕ where η_s is the suspension viscosity and η_0 is the viscosity of pure solvent (Figure 4). The empirical

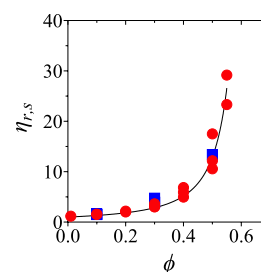


Figure 4. Relative high shear suspension viscosity ($\eta_{r,s}$) as a function of particle volume fraction (ϕ) for suspensions in squalene (red filled circles) and DIDP (blue filled squares). Solid line indicates empirical Eilers' model fit to the experimental data.

Eilers model was used to fit the data and the viscosity of the other DIDP suspensions was estimated.^{38,39} The Eilers model compares the high shear relative viscosity ($\eta_{r,s}$) as a function of ϕ using the equation

$$\eta_{r,s} = \left(1 + \frac{1.25\phi}{1 - \frac{\phi}{\phi_{\max}}} \right)^2 \quad (1)$$

where the random close packing fraction of the spherical colloids is $\phi_{\max} = 0.64$.⁴⁰ Figure 4 shows that eq 1 provides a good fit for the experimental data obtained for both types of

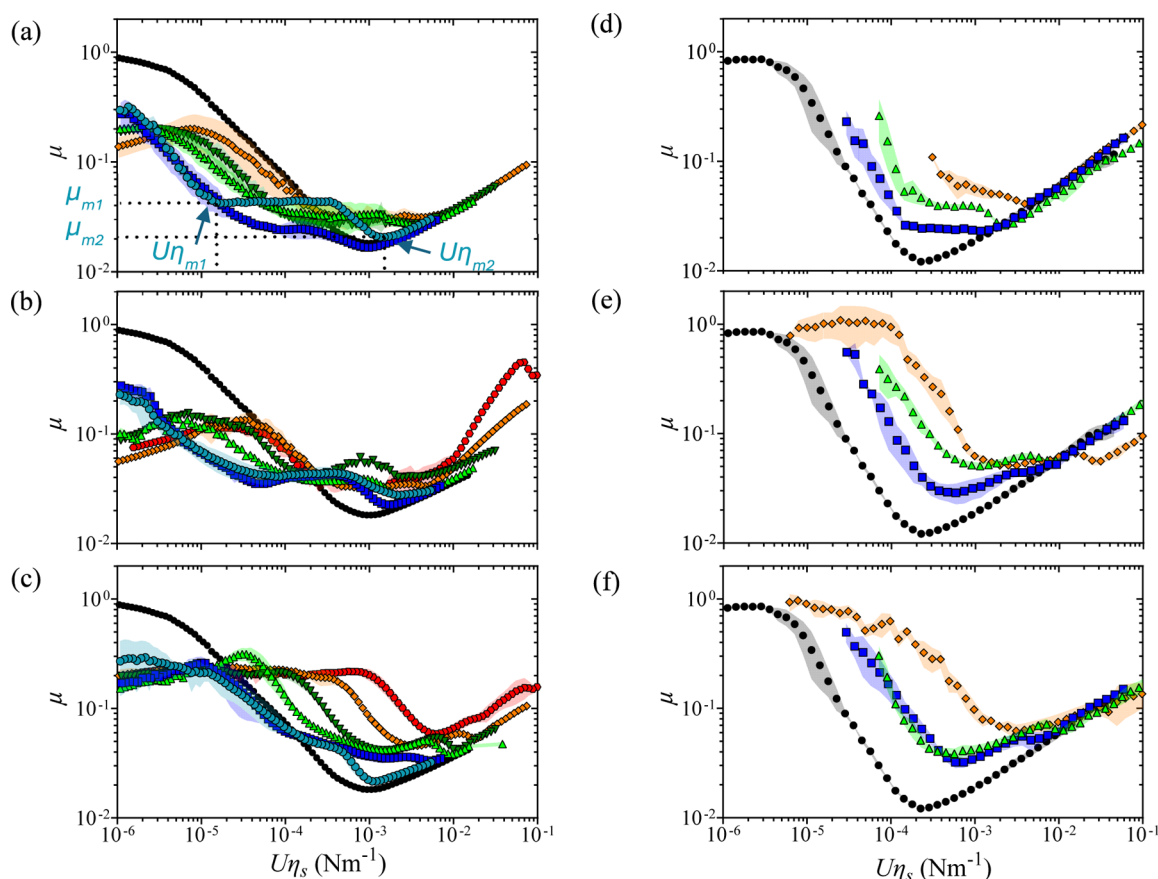


Figure 5. Stribeck curves obtained by shearing suspensions of PMMA particles with diameters (a) $2a = 0.43 \mu\text{m}$ (b) $2a = 1.0 \mu\text{m}$, and (c) $2a = 2.5 \mu\text{m}$ in squalene and (d) $2a = 1.0 \mu\text{m}$ (e) $2a = 2.5 \mu\text{m}$, and (f) $2a = 3.1 \mu\text{m}$ in DIDP. PDMS–PDMS tribopairs are used. Suspension volume fractions (ϕ) used: $\phi = 0.01$ (cyan circle, $\circ$), $\phi = 0.1$ (blue square, $\square$), $\phi = 0.3$ (light green upward triangle, $\triangle$), $\phi = 0.4$ (dark green downward triangle, ∇), $\phi = 0.5$ (orange diamond, $\diamond$), and $\phi = 0.55$ (red hexagon, $\hexagon$). Filled black circles ($\bullet$) represent Stribeck curves obtained with pure squalene in a,b,c and DIDP in d,e,f. Coefficients of friction μ_{m1} and μ_{m2} indicated by dotted lines mark the beginning and end of the mixed regime. The points $U\eta_{m1}$ and $U\eta_{m2}$ represent the beginning and end of the transition point in the extended mixed regime. Color bands represent standard deviation from 3 independent measurements.

suspensions, indicating that the colloidal particles behave nearly as hard spheres in both solvents. Thus, viscosity values η_s extracted from the model are used in our tribological analysis.

Stribeck Behavior

Stribeck curves for the full set of particle sizes, solvent viscosity, and particle volume fraction are plotted against the curve obtained for the pure solvents (black solid circles) in Figure 5. In squalene, the presence of any colloidal particles even down to very low volume fractions of $\phi = 0.01$ decreases the boundary friction (Figure 5a–c), which is seen in the plateau values in μ at slow sliding speeds of $U\eta_s < 10^{-5} \text{ Nm}^{-1}$. Particles are known to reduce the boundary friction, μ_b ; this phenomenon has been previously reported in systems with graphene platelets as additives where boundary friction is reduced through the formation of interfacial films that reduce adhesive interactions.⁴¹ Similarly, soft and hydrated systems make use of deformable hydrogel particles to form a lubricating interfacial layer and redistribute normal stresses within the contact zone.^{42,43} In addition to lubricating tribofilm formation, particles can reduce μ_b through a rolling mechanism when confined between sliding surfaces. For example, gelatin hydrogel microparticles behave as soft ball bearings where a rolling motion of the particles between soft surfaces leads to a

decrease in friction relative to direct sliding ($0.4 \text{ mm/s} < U < 2 \text{ mm/s}$) by reducing interfacial shear during boundary lubrication.⁸ An increase in particle volume fraction (ϕ) causes a decline in μ_b across all particle sizes studied when compared with pure squalene (Figure 5a–c). At dilute concentrations ($\phi = 0.01$), μ_b is higher than the boundary friction of all the other volume fractions investigated, consistent with third-body friction studies where addition of particles affects friction dissipation through localized interactions with surface asperities.⁴⁴ At moderate to high particle concentrations ($\phi \geq 0.3$), a more consistent colloidal lubrication film forms in which particles reside at asperity junctions and act as microscale separators.⁴⁵ Furthermore, as the particle size increases ($2a \geq 2.5 \mu\text{m}$), the point at which μ_b drops (i.e., before m_1) rises to higher sliding speeds ($0.0052 < U \leq 0.073 \text{ m/s}$). The low viscosity of squalene may facilitate rolling dominated mechanisms at moderate ϕ , while the gap may be persistently larger at high ϕ which consistently reduces the boundary friction.

The EHL regime for most suspensions generally falls on the same line as that of the pure solvent when accounting for the effect of η_s , indicating that the suspension viscosity correctly describes EHL behavior with some deviations found only at high volume fractions ($\phi = 0.5$ and 0.55 for $2a = 1 \mu\text{m}$ in squalene). The noncollapse in the ML regime is consistent

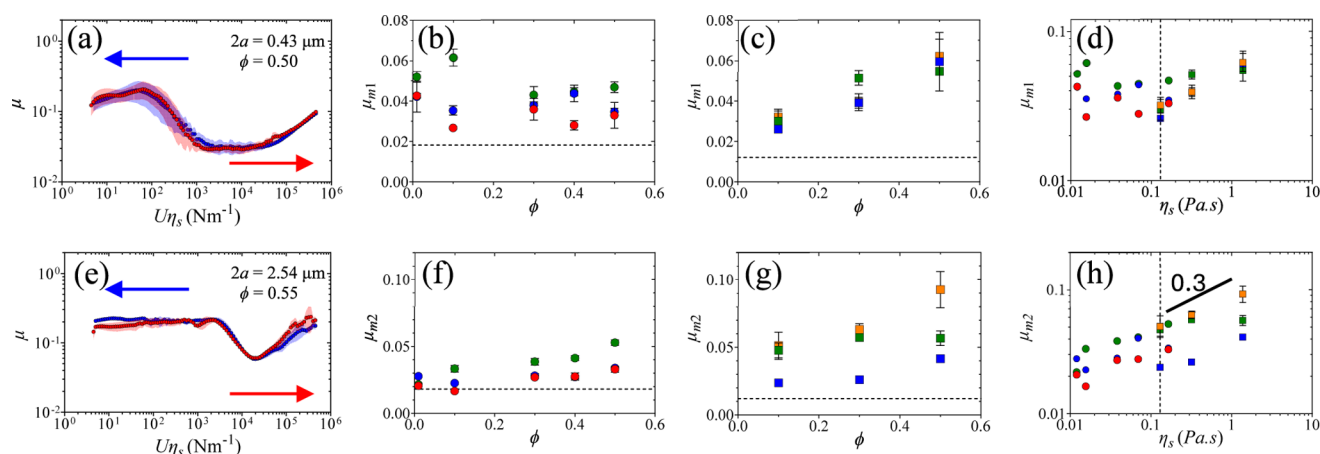


Figure 6. Representative Stribeck curve hysteresis experiments using (a) $2a = 0.43 \mu\text{m}$ $\phi = 0.5$ and (e) $2a = 2.5 \mu\text{m}$ $\phi = 0.55$ particles suspended in squalene. Upward velocity sweep (red) and downward velocity sweep (blue) are shown. Friction coefficient at the onset and termination of the mixed regime (μ_{m1} and μ_{m2}) with increasing volume fraction (ϕ) in (b, f) squalene (filled circles) and (c, g) DIDP (filled squares) respectively. (d) Onset (μ_{m1}) and (h) termination (μ_{m2}) mixed regime friction coefficient with increasing suspension viscosity in squalene (filled circles) and DIDP (filled squares) respectively. Particle diameters are $2a = 0.43 \mu\text{m}$ (red), $1.0 \mu\text{m}$ (blue), $2.5 \mu\text{m}$ (green), and $3.1 \mu\text{m}$ (orange). The error bars indicate the standard deviations from 3 independent measurements. Dotted lines represent the friction coefficient at transition for pure solvent in b, c, f and g.

with a breakdown of the continuum approximation once particles are present. Scaling with U alone produces a better ML regime collapse here, because viscous effects are less important at the onset of the transition, which is governed primarily by the geometric relationship between the interfacial gap and particle size rather than by hydrodynamic forces alone. Hydrodynamic lift may still contribute to surface separation, but the onset of the extended ML regime occurs when the resulting gap becomes comparable to the particle diameter. We nonetheless retain $U\eta_s$ as the plotting axis throughout, as it remains the conventional parameter in the literature and correctly captures EHL behavior. Recall that we define η_s only in the Newtonian plateau regime (Figure 2). At higher ϕ and U values, dense colloidal suspensions are known to undergo shear thickening in which the suspension viscosity diverges with increasing shear stress and shear rates.⁴⁶ The shear thickening effect is not accounted for in η_s and is likely causing the deviation in the EHL regime ($U\eta_s > 0.0095 \text{ N m}^{-1}$).

There is an extended ML regime between the boundary and EHL regime when particles are present (Figure 5 a–f), represented by a range of conditions where the value of m stays relatively constant across a range of sliding speeds, similar to the elastoviscous regime observed in the sliding of articular cartilage.³⁰ This broad transition regime does not exist for the Stribeck curves of pure solvents, and is present in colloids of smaller particle sizes, where particles of $2a = 0.43 \mu\text{m}$ produce the most pronounced extended zone at the lowest volume fraction of $\phi = 0.01$. The extended ML regime effect persisted when DIDP was used instead of squalene. We demarcate the velocities of extended ML regime by $U\eta_{m1}$ and $U\eta_{m2}$, along with their corresponding friction coefficients by μ_{m1} and μ_{m2} . A few of the curves exhibit micro-EHL transitions within this extended ML plateau, potentially due to particles becoming embedded inside the PDMS surfaces and increasing the effective mesoscale roughness of the surfaces.²¹ The magnitudes of μ_{m1} and μ_{m2} also increase with $2a$ and ϕ , suggesting that the lubrication film thickness is supported by a combination of the particles that physically bridge the gap as well as the viscous effect provided by the suspensions. In the

sections below, detailed analysis of the correlations of μ_b , μ_{m1} , μ_{m2} , U_{m1} , and U_{m2} with $2a$ and ϕ is used to generate a mechanistic insight of this extended ML regime. At higher particle sizes, boundary lubrication becomes more dominant (Figure 5 c,f). The developed rough interface from the particles with larger $2a$ interacting with the PDMS tribopairs might be responsible. It is possible that the size causes an exclusion of the solvent when creating the lubrication gap. This in turn makes the friction mechanism more particle dominated with a ball bearing effect in action.

Effect of Volume Fraction and Particle Size on Mixed Lubrication Regime

To establish that the volume fraction and particle size of our suspensions, rather than the strain history of accumulated sliding, are responsible for the observed mixed lubrication transitions in Figure 5, we performed up–down hysteresis experiments on two representative conditions in squalene (Figure 6a, e). In these experiments, the sliding velocity was increased from low to high values and subsequently decreased over the same range. The resulting Stribeck curves overlap closely between the ascending and descending sweeps across all lubrication regimes, including both transition velocities of the extended mixed regime (U_{m1} and U_{m2}), confirming that the transitions are governed by hydrodynamic lift and particle confinement within the gap rather than by cumulative sliding history. This reversibility further indicates the absence of irreversible particle entrapment or permanent embedding into the compliant PDMS surfaces, and that no significant wear of the PDMS tribopairs occurs during testing as the measured friction coefficients remain comparable. We therefore proceed to evaluate the influence of particle volume fraction and particle size on the onset and termination of the extended mixed lubrication regime.

The viscosity of the solvent changes the behavior of μ_{m1} substantially, where suspensions prepared in squalene showed μ_{m1} values that are independent of particle size and volume fraction, while suspensions prepared in DIDP, which is of much higher viscosity, showed μ_{m1} values that increase with increasing volume fraction. Figure 6b shows that in squalene,

μ_{m1} remains close to 0.04 ± 0.02 across all particle sizes and volume fractions tested. Figure 6c shows that μ_{m1} increases with volume fraction in DIDP with nearly negligible dependence on the particle diameters. For all suspensions prepared at $\phi = 0.5$ in DIDP, there is an increase in μ_{m1} when compared to the minimum in the friction coefficient from the Stribeck curve of the pure DIDP solvent ($\mu_{m1} = 0.059 \pm 0.009$).

Friction Coefficient Evolution at the Onset of the Extended Mixed Lubrication Regime (m_1)

The weak dependence of μ_{m1} with viscosity for suspensions prepared in squalene and the corresponding strong dependence for those in DIDP suggest that the hydrodynamic contributions from the suspension viscosity plays a major role in maintaining a constant gap height when the sliding speed is increased and specifically, that the particles in the suspensions contribute to the maintenance of this gap in different ways depending on the value of η_s . Figure 6d is a log–log plot of all data points, showing a distinct point near $\eta_s = 0.1$ Pa·s where the scaling of μ_{m1} changes from being independent of η_s to increasing with η_s . Since μ_{m1} marks the beginning of the extended ML regime, we speculate that a thin lubrication film containing particles already exists within the gaps. These particles may be embedded within the PDMS when the suspension viscosity is low in the case of squalene or freely suspended within the gap in the case of DIDP due to a higher lubrication pressure. A similar entrapment mechanism has been reported by Rudge et al., who found that in compliant elastomer contacts lubricated with low viscosity suspensions ($0.001 \text{ Pa}\cdot\text{s} < \eta < 0.04 \text{ Pa}\cdot\text{s}$), the friction coefficient of the system containing particles is similar to that of systems containing only pure solvent, effectively reducing the particles' hydrodynamic contribution and influence on friction.¹⁸ The hydrodynamic pressure generated within the contact is insufficient to develop a lift and overcome the confinement of particles from elastic deformation. This low pressure minimizes particle transport and entrainment from the gap. The predicted film thickness thus remains smaller or comparable to the particle diameter. Since only the solvent is able to flow through the contact gap, friction is governed primarily by pure solvent rheology and substrate compliance rather than by particle size or volume fraction. With pure squalene having a viscosity in the range of $0.01 \text{ Pa}\cdot\text{s}$, at low velocities U_{m1} , μ_{m1} does not change significantly with particle size or the suspension viscosity. In other words, the particles are embedded within the compliant PDMS–PDMS and only the squalene solvent flows through the gap at these low sliding speeds, and therefore changing particle properties do not significantly alter the friction response.⁴⁷ For the other case where suspensions are prepared in DIDP, the increased hydrodynamic effects from the higher solvent viscosity and correspondingly higher η_s values generate a higher pressure in the gap ($\approx 10^3$ – 10^4 Pa). Here, the suspension acts as a continuum and therefore the friction coefficient increases with increasing ϕ and η_s .

A linearly increasing relationship between μ_{m1} and particle volume fraction exists with suspensions prepared in DIDP as shown in Figure 6c. Unlike squalene, where particles remain mechanically excluded from the contact gap at low velocities, DIDP enhances the particle entrainment and flow of particles within the gap at these velocities ($U = 0.0020 \pm 0.0013 \text{ m/s}$), thereby increasing the effective shear resistance in the contact zone. Particle crowding becomes important as the system aims

to achieve complete hydrodynamic lift of the surfaces, which likely causes the rise in μ_{m1} . The higher viscosity of DIDP promotes greater particle inclusion within the lubricating film, where the particles are now allowed to move in and out of the contact zone which facilitates a partial hydrodynamic lift to create a more effective load-bearing mechanism.

Friction Coefficient Changes at the Termination of the Extended Mixed Lubrication Regime (m_2)

Figure 6f, g show a similar trend in which μ_{m2} shows a modest increase with ϕ and $2a$ for suspensions prepared in squalene, and a greater increase for suspensions prepared in DIDP. Suspensions with the lowest ϕ values ($\phi = 0.01$) generate Stribeck curves that are the most similar to that of the pure solvent. As the particle diameter and ϕ increases, the values of μ_{m2} start to become significantly greater than that of the pure solvent. The transition value of μ_{m2} can be thought of as the ratio of shear and normal forces at which a full lubrication film begins to develop, at speeds just below that of a standard EHL transition. At these speeds, the hydrodynamic forces that lift the surfaces from each other are strongly influenced by the suspension viscosity. The friction coefficient at this point scales linearly with the film thickness and the suspension viscosity and is no longer dependent on solid–solid contact between the PDMS tribopairs. Since suspensions prepared in DIDP have higher viscosity values than those in squalene, naturally, they will generate higher friction coefficients because μ_{m2} depends directly on the viscosity.

In squalene-based suspensions (Figure 6f), the range of μ_{m2} ($0.017 < \mu_{m2} < 0.053$) remains close to the EHL transition friction coefficient of the pure solvent (0.018). Consider the picture we drew in Figure 1 where μ_{m2} indicates that the system is approaching full film formation. Here, hydrodynamic lift increasingly governs load support which suppresses particle-induced structuring and thus, minimizes the effect of particles on the overall frictional response. Figure 6f shows that even though particles are present in squalene, the dependence of μ_{m2} on $2a$ and ϕ is fairly negligible except at very large ϕ values, suggesting that hydrodynamic pressure effectively screens any microstructural effects unlike in the case of μ_{m1} , where particles may be completely entrained and only the solvent passes through the gap. DIDP has a higher base viscosity and leads to a larger increase in μ_{m2} ($0.024 < \mu_{m2} < 0.093$) with ϕ especially for larger particles ($2a \geq 2.5 \mu\text{m}$) (Figure 6g). In this mixed EHL regime, the lubrication film should be near fully developed, asperities on the PDMS surfaces would be relatively far apart from one another, and particles should be entering the gap fully and the suspension should behave as a continuum.

The hypothesis that a full hydrodynamic film is generated at the end of the mixed regime (marked by m_2 in Figure 1) is further supported by plotting the value of μ_{m2} against h_s for both lubricants in Figure 6h, which shows that μ_{m2} is an increasing function of the suspension viscosity with a scaling exponent of 0.3. Assuming that the normal load is held constant and fully developed Couette flow between the tribopairs, and that the velocity of the top tribopair surface is constant at U , lubrication equations state that the shear force is $F_s \sim \eta_s UA/h$, where A is the contact area.^{17,19} In soft EHL contacts, Hamrock and Dowson showed that $h \sim (\eta_s^{2/3} F_N^{-2/9})$.⁴⁸ Therefore, when we substitute the Hamrock–Dowson scaling into lubrication scaling under fixed load conditions to get $\mu \sim (\eta_s UA)/(hF_N)$, scaling analysis shows that μ_{m2} should scale sublinearly with the suspension viscosity

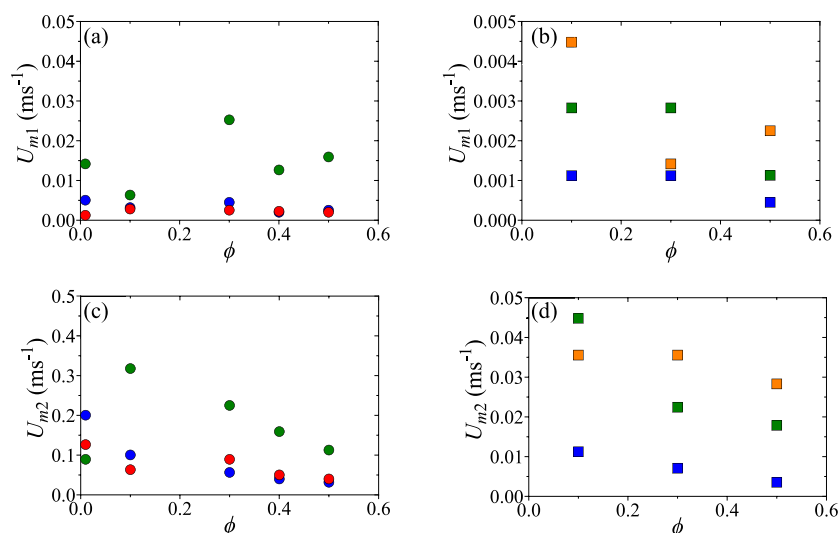


Figure 7. Sliding speed at the onset and termination of the mixed regime transition (U_{m1} and U_{m2}) changes with increasing volume fraction (ϕ) in (a,c) squalene (filled circles) and (b,d) DIDP (filled squares). Particle diameters are $2a = 0.43 \mu\text{m}$ (red), $2a = 1.0 \mu\text{m}$ (blue), $2a = 2.5 \mu\text{m}$ (green), and $2a = 3.1 \mu\text{m}$ (orange).

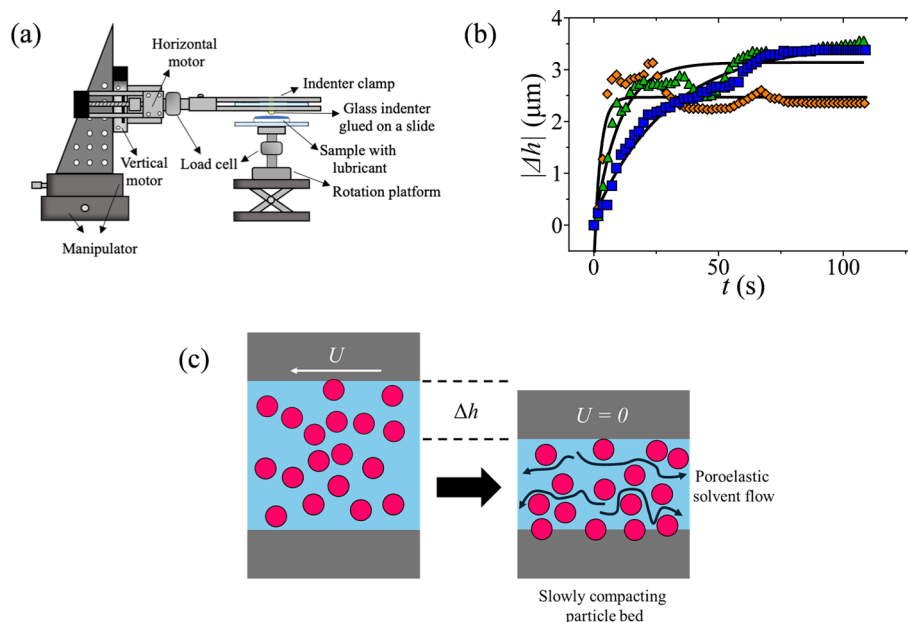


Figure 8. (A) Schematic of the slide-and-stop indentation method apparatus used to measure changes in the lubricant film thickness. (b) Absolute change in the indenter vertical position $|\Delta h|$ as a function of time during the relaxation experiment. Solid lines are exponential fits. (c) Illustration of the height change from particle relaxation after cessation of shear. In (b, c), particle diameters include $2a = 1 \mu\text{m}$ (blue square, $\square$), $2a = 2.5 \mu\text{m}$ (green upward triangle, $\triangle$), and $2a = 3.1 \mu\text{m}$ (orange diamond, $\diamond$). All data sets are from suspensions prepared in DIDP at $\phi = 0.50$.

($\mu_{m2} \sim \eta_s^{1/3}$). The exponent of 0.3 obtained from our data in Figure 6h indicates that, indeed, a full EHL film develops at the end of the mixed lubrication transition point and that particle-induced stresses are small compared to hydrodynamics.

The transition between boundary friction and ML occurs when sufficient solvent enters the contact gap, while the transition between ML and EHL occurs when the lubrication film becomes thicker than the asperities on the tribopair surfaces and where the entire suspension, not just the solvent, can be treated as a viscous continuum and modeled accurately with Reynolds equations. Thus far, the picture in Figure 1 suggests that the plateau in the ML regime arises from a separation of the solvent and the particles entering the gap. At m_1 , the conjecture is that the gap height h should be on the

order of the roughness on the PDMS surfaces and that only the solvent molecules can pass through. The role of the solvent is therefore to provide sufficient hydrodynamic separation of the surfaces until higher velocities (U_{m2}), where a mixture of particles and solvent can now enter the gap.

Figure 7a shows that U_{m1} remains fairly independent of ϕ in suspensions of squalene, with larger U_{m1} values and fluctuations seen with larger particles ($2a = 2.5 \mu\text{m}$). These results indicate that the first ML transition point does not depend very much on the presence of particles when squalene is present, and that particles are likely embedded in the PDMS matrix and only solvent is able to flow through the extremely small and compliant gap. Therefore, the velocity of this transition holds steady regardless of ϕ or $2a$. In contrast,

Figure 7b shows that increasing ϕ in suspensions of DIDP causes U_{m1} to decrease. Since DIDP is nearly 100 $\times$ more viscous than squalene, it may generate a slightly larger gap at m_1 and therefore some particles can already enter the contact area. Hamrock and Dowson equations predict that $h \sim (\eta_s U)^{2/3}$. When the height is set as a constant, the velocity of the fluid will decrease if the viscosity is increased. Hence, the observation that U_{m1} decreases with increasing ϕ in DIDP suggests that some lubrication effects are already at play, and the dependence with ϕ is only possible due to the increasing suspension viscosity due to the ability of particles to enter the gap. The magnitudes of U_{m1} are also $\sim 10\times$ larger for squalene than for DIDP, perhaps because the particles are more entrained with a low viscosity solvent and a higher velocity is required to generate some lift to allow more solvent to flow into the gap.

Figure 7c and d show that the downward trend in U_{m2} with increasing ϕ is found in both types of suspensions. At this point, lubrication films are becoming fully developed and able to separate the PDMS tribopairs completely from each other. The velocity of this transition can only decrease if the entire suspension enters the gap. Since $\eta_s \sim \phi^2$ (Figure 4), if we consider that there is a critical h at which EHL begins to occur, then U_{m2} must necessarily decrease to maintain this gap height if lubrication equations hold.

We choose to only show U_{m1} and U_{m2} as the dependent variables in Figure 7 instead of multiplying it by the suspension viscosity because it better illustrates the important role of lubrication beyond that of the viscosity. Plots of both $\eta_s U_{m1}$ and $\eta_s U_{m2}$ against ϕ show increasing trends because the suspension viscosity dominates ($\eta_s \sim \phi^2$) at higher particle loading. They are also similar in magnitude for both systems tested across all ϕ values ($0.0005 \text{ N m}^{-1} < \eta_s U_{m1} < 0.003 \text{ N m}^{-1}$, $0.001 \text{ N m}^{-1} < \eta_s U_{m2} < 0.03 \text{ N m}^{-1}$), which indicates that the suspension viscosity is important in generating a large EHL lift. Overall, these results are in agreement with the mechanistic framework shown in Figure 1.

Relaxation of Lubrication Film on Cessation of Sliding

We first characterized the relaxation behavior of the suspension confined between a fixed PDMS slab and a sliding PDMS indenter under normal loading (Figure 8a). As described in the Methods section, PDMS substrates were initially coated with a thin film of DIDP particle suspension, which served as the lubricant, and then placed on a glass slide mounted on a rigid metal plate. A PDMS indenter was lowered into contact with the lubricated substrate and slid laterally across the surface at a prescribed speed under a fixed normal load, while the vertical displacement of the indenter was continuously recorded. Sliding was performed over a distance of 12 mm, after which the motion was stopped abruptly to initiate the relaxation phase. The duration of this phase was recorded and defined as the relaxation time.

At the end of the sliding stage, the system relaxes (the film thickness decreases) as the applied normal load drives liquid out of the contact region. Just before the end of the sliding phase, the vertical position of the indenter was recorded as h_1 . After the subsequent relaxation, it was recorded as h_2 . The change in distance was $\Delta h = h_1 - h_2$. This displacement reflects contributions from the lubricant film thickness and the substrate's deformation. To exclude the influence of the substrate deformation and extract the film thickness for the DIDP system, the glycerol lubricant system was used as a

reference. Under these experimental conditions, the film thickness for the glycerol was negligible compared with the DIDP case. Thus, the film thickness for DIDP systems $h_{\text{DIDP}} = \Delta h_{\text{DIDP}} - \Delta h_{\text{glycerol}}$. The corrected heights are then denoted as h_0 at the moment when the indenter stops sliding and h_f after relaxation. At $U = 2.0 \times 10^{-4} \text{ m/s}$, a normal force of 152, 120, and 169 mN was applied when using DIDP suspensions of $2a = 1.0 \mu\text{m}$, $2a = 2.5 \mu\text{m}$, and $2a = 3.1 \mu\text{m}$ respectively. $\phi = 0.5$ was kept constant for all particle diameters.

These experiments were conducted to infer the degree of particle entrainment within the extended mixed-lubrication regime, which influences the gap height between the PDMS tribopairs. Specifically, we monitored the change in lubrication-layer thickness, Δh , that developed as the indenter moved at constant sliding speed across the substrate and subsequently relaxed after sudden cessation of motion. The normal load used in the relaxation experiments was selected based on the end of the extended mixed lubrication regime, denoted as m_2 in the Stribeck curves shown in Figure 5.

Figure 8b plots the change of Δh over time of the relaxation stage (relaxation starts at $t = 0 \text{ s}$) and reveals that Δh changes with time following a shifted exponential first-order decay, $\Delta h = -(h_0 - h_f)\exp^{-t/\tau} + h_f$ where h_0 is the height at the moment when the indenter stops sliding, h_f is the height of the film after relaxation, t is the time and τ represents the relaxation time. The values of these parameters for suspensions comprising $2a = 1.0 \mu\text{m}$, 2.5 and $3.1 \mu\text{m}$ particles in DIDP are shown in Table 1. The fluid film relaxes more rapidly with

Table 1. Fitting Parameters Used to Obtain Relaxation Times From Indenter Experiments

	particle diameter ($2a$)		
	1 μm	2.5 μm	3.1 μm
$h_0 - h_f$ (μm)	3.34	3.25	3.27
h_f (μm)	3.49	3.14	2.47
τ (s)	30.11	9.98	2.52

suspensions of larger particles. The relaxation is likely to arise from solvent poroelastic flows between the solid particles upon cessation of shear, and less likely due to Brownian relaxation of these particles. The empirically observed scaling $\tau \sim a^{-1}$ cannot be explained by Brownian relaxation time scales, which have a scaling $\sim a^3$. Instead, we suspect that the solvent fluid is likely to escape from the contact gap as poroelastic flow through embedded solid particles. If we consider Darcy flow with the Kozeny–Carman closure for permeability k in a randomly packed stationary bed of spheres, then $k \sim a^2$, and therefore the superficial velocity of fluid through the interstitial pores would scale as $U_{\text{fluid}} \sim k \sim a^2$.^{49,50} In other words, the larger the particle size, the larger the pores and therefore the solvent liquid drains more rapidly ($\tau \sim U_{\text{fluid}}^{-1} \sim a^{-2}$).

If we consider that the postcessation height drop is on the order of a few particle diameters as shown in Figure 8b, then the solvent is likely not just draining through a fixed porous geometry but rather through a combination of squeeze flow and poroelastic compaction. In other words, the suspension lubricant enters a short-lived consolidation regime, where the film thickness decreases due to the poroelastic settling of a dense particulate bed while the interstitial solvent is squeezed out over most of the contact area (Figure 8c). The transient densification of the bed could lead to dynamic changes in the

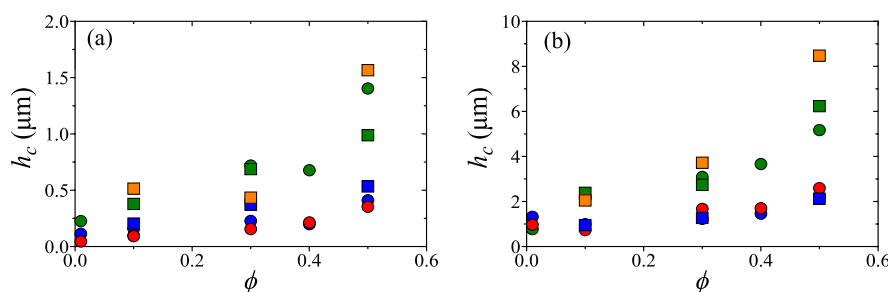


Figure 9. Central film thickness (h_c) estimated from the Hamrock–Dowson model at the beginning of transition μ_{m1} and (b) for the end of transition μ_{m2} for suspensions in squalene (filled circles) and DIDP (filled squares). Diameters for colloids in the suspensions: $2a = 0.43 \mu\text{m}$ (red), $2a = 1.0 \mu\text{m}$ (blue), $2a = 2.5 \mu\text{m}$ (green), and $2a = 3.1 \mu\text{m}$ (orange).

pressure drop, drainage length scale, and k as a function of time. These coupled geometry and flow effects could reduce the Darcy flow to a $\tau \sim a^{-1}$ scaling. Further investigations, not within the scope of this work, that involve direct visualization of the contact gap during relaxation will be necessary to identify the precise mechanism for the drainage time scale.

Gap Height Evolution with Particle Concentration

The absolute lubrication film thickness is challenging to measure due to the difficulty in visualization as well as variability in material properties at the contact zone, and we are unable to measure it directly through the indentation experiments. As discussed earlier, the EHL fluid film is formed as the speed between the tribopairs increases and hydrodynamic lift generated by lubricant pressure becomes significant. We cannot directly measure the absolute dynamic film thickness of the tribopairs which is a well-known challenge in soft tribology with compliant elastomer substrates. It should be noted that optical measurements of lubricant film thickness have been successfully demonstrated in related elastomeric contacts using transparent counterfaces, including fluorescence imaging of radial lip seals, interferometry in rubber seals, and laser-induced fluorescence mapping in elastomer contacts.^{51–53} Therefore, to test whether the particle exclusion is consistent with the observed Stribeck transitions, we estimate the gap height at the sliding speeds corresponding to m_1 and m_2 using the modified Hamrock–Dowson equation for central film thickness h_c as shown in eq 2.^{21,48}

$$h_c = 11.15(U\eta_s)^{2/3}F_N^{-2/9}E'^{-4/9}\left(\frac{R_{ball}}{2}\right)^{7/9}(1 - 0.72e^{-0.28k}) \quad (2)$$

where E' denotes the reduced Young's modulus of the tribopair, R_{ball} is the radius of the PDMS sphere (6.35 mm), and k represents the aspect ratio of the elliptical contact area. In this study, we assume that $k = 1$ which corresponds to circular contacts. The modified equation was used to account for the low elastic modulus of the PDMS tribopair and to provide us with a measure of the load-bearing capabilities of the developed film in separating the contacting surfaces. We are also able to determine the height of the film relative to the particle diameter as this could provide information on the friction modulation mechanism. The central estimate provides a practical means of connecting our experimental observations to classical EHL theory and of assessing whether the measured transitions are consistent with the formation of a fully developed lubrication film.

Figure 9a,b shows the estimated central film thickness (h_c) from the Hamrock–Dowson model at the beginning (m_1) and

end (m_2) of the extended ML regime for squalene and DIDP suspensions. In both solvents, the predicted film thickness increases from m_1 to m_2 across all particle sizes and volume fractions investigated in a way that is commensurate with the way the suspension viscosity increases with ϕ , shown earlier in Figure 4. Nevertheless, h_c also shows a dependence with $2a$, where the values of h_c are generally greater for suspensions containing larger particles ($2a = 2.5$ and $3.1 \mu\text{m}$).

At m_1 (Figure 9a), the gap height h_c remains smaller than the particle diameters across all experiments, suggesting that particles cannot be completely suspended in a continuous hydrodynamic layer but instead, elastic deformation of the PDMS surfaces permits partial particle embedding and direct asperity-particle contact which maintains a low h_c to reduce the amount of liquid that enters the gap. Because hydrodynamics does not change significantly in this regime, the friction coefficient remains relatively constant with increasing sliding speeds without the system transitioning into EHL. Figure 9b shows that at point m_2 , h_c increases with ϕ in both squalene and DIDP suspensions, but the underlying mechanisms differ due to the effective suspension viscosity η_s . In both cases, higher ϕ raises η_s and from the scaling in eq 2, a thicker film is predicted. This scaling supports our earlier argument in Figure 6h that higher viscosity of DIDP amplifies the hydrodynamic lift and therefore produces a more continuous ML film. However, it is important to recognize the limitations of the Hamrock–Dowson model, which was originally formulated for fully flooded, isothermal, smooth contacts lubricated by a homogeneous Newtonian fluid, relying on idealized material properties and steady state conditions.⁵⁴ In soft, particle-loaded tribology systems, several deviations from these assumptions arise. First, the lubricating medium is no longer homogeneous but consists of a dense suspension, where the deformable surfaces and finite particle sizes ($h \sim 2a$) can lead to entrainment effects that are not explicitly described in the Hamrock–Dowson framework. Second, the gap height h has a component that is related to the drainage of fluid through a compacting poroelastic bed. To reconcile Hamrock–Dowson estimates with experiments, theoretical development should include correction factors for geometric confinement and poroelastic flows.

Future Outlook

Several open questions remain that motivate future experimental and modeling work. A key assumption throughout this study is that the bulk volume fraction ϕ is uniform and equal to the local volume fraction at the contact zone. However, as our schematic in Figure 1 illustrates, ϕ is expected to be spatially heterogeneous in the contact zone. Since η_s is highly

sensitive to ϕ at high volume fractions, the local viscosity governing friction may differ substantially from the bulk value used in our analysis, and this potential discrepancy must be carefully considered. Directly resolving the local volume fraction in the contact zone (ϕ_{contact}) as a function of sliding speed across the boundary, ML, and EHL regimes would require a confocal tribology setup combining fast-scanning fluorescence microscopy with the tribological geometry used in this study. Such measurements, which are beyond the scope of the current work, could provide a direct experimental test of the particle exclusion picture at m_1 and m_2 and allow us to investigate regime-specific local viscosities rather than inferring from bulk measurements, and are therefore likely to be important in advancing quantitative understanding of particle-laden soft tribological systems.

CONCLUSIONS

Particle-laden lubricants provide a powerful strategy for modifying frictional behavior in soft tribological systems by introducing an extended ML regime that is absent in molecular fluids. Systematic variation of the particle diameter and volume fraction reveals two transition points, m_1 and m_2 , that define the extended ML regime and capture the evolving balance between particle confinement, entrainment, and hydrodynamic lift. In squalene, the low-viscosity solvent, particle entrainment is substantial due to the soft PDMS contacts, and friction at m_1 is governed by solvent flow through a confined contact area. Suspensions prepared in DIDP promote sustained particle presence within the contact due to a higher solvent viscosity, leading to a stronger dependence of friction on particle concentration. Reynolds' lubrication scaling and film thickness estimates show that the transition to the EHL regime is consistent with flows driven primarily by viscous dissipation, while at lower sliding speeds and moderately high particle volume fractions, geometric compaction and poroelastic flows generate time-dependent changes in the gap height that are not accounted for in classical Hamrock–Dowson models. These findings establish particle entrainment and suspension rheology as key design parameters for tuning wet friction between soft substrates and provide a framework for extending the ML regime across a broader range of sliding conditions in soft material systems. It should be noted that the extended ML regime does not universally yield the lowest possible friction coefficient. For low-viscosity suspensions prepared in squalene, the ML plateau friction remains comparable to the pure solvent EHL minimum, while in high-viscosity solvents such as DIDP, viscous contributions from the entrained suspension elevate friction above the pure solvent EHL minimum at moderate to high volume fractions. The primary tribological benefit of the extended ML regime is therefore the stabilization of surface separation and the minimization of solid–solid wear across a wider range of operating conditions.

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Notes

The authors declare no competing financial interest.

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