Deformation and friction of MoS$_2$ particles in liquid suspensions used to lubricate sliding contact

Rashmi R. Sahoo, Sanjay K. Biswas *

Department of Mechanical Engineering, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT

Tribology of a well known solid lubricant molybdenum disulphide is studied here in water and oil medium, over a large range of contact dimensions. Lateral force microscopy is used to identify the deformation modes; intra-crystalline slip, plastic grooving, fragmentation and fracture, of single particles. The medium and agglomeration were found to dictate the deformation mode. Steel on steel tribology lubricated by suspensions of these particles in liquid media was conducted over a range of contact pressure and sliding velocity. A scrutiny of the frictional data with the aid of Raman spectroscopy to identify the transfer film, suggested that the particle size, as it is at contact, is an important tribological parameter. Ultrasonication of the suspension and dispersion of the particle by surfactants were used to control the apriori particle size fed into the suspension. Correspondence of friction data of the gently sonicated suspension with that of the ultrasonicated suspension with dispersants indicated the importance of liquid ingestion by these particles as it controls their mode of deformation and consequent tribology.

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1. Introduction

In sliding tribology, to impart boundary lubrication properties to a lubricant, beneficial products of reaction between the metal parts and the antinear and extreme pressure additives such as molybdenum dialkyldithiocarbamate and zinc dithiophosphate are generated in-situ. A 'non-reaction' route is to allow functionalization of the solid surface by organic molecules dispersed in the liquid lubricants. These molecules however have limited load bearing capacity and thermal stability. Alternatively, to make up a lubricant, there has been an attempt, in the recent times, to suspend nanoparticles of inorganic materials such as MoS$_2$ and WS$_2$ [platelets of the 2H polytype] as additives in base liquids such as oil or water [1,2]. These solid particles, generally of a layered structure shear easily under traction to yield low friction. The particles provide load bearing strength to the lubricant and have a high thermal stability. The suspensions have been found to be good boundary lubricants [3–7].

Metal dichalcogenides of the form MX$_2$ (M = W, Mo; X = S, Se) are low friction materials which under traction undergo basal plane slip [8,9], M–X atoms in layers bind covalently in hexagonal arrays while the layers bind with each other by weak van der Waals forces. The unit cell has hexagonal symmetry and includes two adjacent lamellae (2H arrangement). The coefficient of friction of these materials is low as low shear forces are required to cause intercrystalline slip in the weak interplanar region.

The principle mechanism of boundary lubrication using nanoparticles as additives is distinctly different from that when organic surfactants are used as additives. When the additive is a nanoparticle, the liquid transports these particles, randomly dispersed in the liquid, to the region of contact between the asperities of mating surfaces [10]. The solid particle surfaces adhere to the asperities and on sliding a plane of weak shear develops within the particles [11–13] while the elastic or plastic strength of the solid particle supports the normal load. Thin films of these particulate materials grow on mating the surfaces as material is transferred and back transferred [14] to develop a regime of low friction steady state tribology. The mechanism is particularly attractive when the liquid is water [15–18]. Water has a poor pressure–viscosity index which allows minimal load support by the liquid, unlike in the case of oils.

The main problem in implementing the above mechanism for a practical application is agglomeration. The small particles because of their large surface area to volume ratio are easily attracted to each other to form agglomerates. Such agglomerates are not easily accommodated in the contact zone and the beneficial effect of the layered structure is lost. It has been shown [19–22] that agglomerates promote poor tribology. If they can be transported to the contact, it is the bulk isotropic properties as opposed to the interlayer shear properties which are invoked to account for dissipation.
Dispersants therefore play a major role in lubrication where nanoparticles are used as additives. Organic dispersants have a polar functional group attached to a long bulky hydrocarbon group. They utilize oxygen and/or nitrogen polarity and do not contain metal ions. This enables them to adsorb on the particles and keep them in suspension so that they do not agglomerate. Organic dispersants are adsorbed by these particles suitably to generate a repulsion force regime between the particles to act against the natural attraction between the particles. Such repulsive barriers may be electrostatic or entropic. In this study we use poly isobutylene succinimide (PIBS) and cetyl trimethyl ammonium bromide (CTAB) for dispersing MoS2 particles in hexadecane and water, respectively.

The dissipation mechanism of layered MoS2 single particles under traction in the ambient is well understood. Here we are concerned with the tribology of these particles in liquid suspension. We explore in this paper the deformation and dispersion of monolithic and agglomerated particles in oil and water suspension and show how such suspensions when used as lubricants in steel on steel sliding contact influence friction.

2. Experimental details

2.1. Materials

Polycrystalline EN-31 steel (carbon 1%, manganese 1.1%, silicon 0.1%, phosphorous 0.05%, sulfur 0.05%, chromium 1%, rest iron) and stainless steel (SS 304) are used as substrates in our tribological experiments for hexadecane (HD) and water suspensions respectively. The layered MoS2 particles were procured from Alfa Aesar MA, USA (2 μm average particle size, monolithic particle) and Lowerfriction Lubricants, M. K. Impex, Canada (MK-MoS2-N3050, agglomerates consist of 50 nm MoS2 crystallites). Hexadecane (∼99%, Sigma-Aldrich) is used as the base oil for lubricated tribology (particles suspended in hexadecane). Water used for particle suspension is prepared using a Milli-Q system (Milli-Q Integral 3 Pure, Millipore Aldrich) is used as the base oil for lubricated tribology (particles suspended in hexadecane). Water used for particle suspension is prepared using a Milli-Q system (Milli-Q Integral 3 Pure, Millipore SAS, France) containing ion exchange and charcoal stages resulting in a conductivity less than 1 × 10⁻⁶ S/m.

2.2. Preparation of samples for Atomic Force Microscopy (AFM) and microtribometry tests

A suspension of particles was prepared with 20 mg of monolithic and agglomerated MoS2 particles in 10 ml n-hexane (99.8% pure, S.D. fine chemicals limited, Mumbai) solution and sonicated for 15 min. For high load experiments, a drop of the suspension is spin coated on a 10 mm × 10 mm × 0.5 mm square p-type silicon wafer (100) substrate and spin coated at a rotational speed of 400 rpm. A drop (2% w/v) of polymethyl methacrylate (PMMA, Mol. Wt. ∼ 495,000) dissolved in chloroform (CHCl3, 99% pure, S.D. fine chemicals limited, Mumbai) is poured on the silicon wafer (100) substrate and spin coated at a rotational speed of 400 rpm. The sample is then heated in an oven, kept at 150 °C for 1 h to melt the PMMA so that it can spread uniformly over the whole silicon wafer substrate. This is done to attach the MoS2 particles on the substrate and the PMMA acts as glue between the particles. The sample after being taken out from the oven is rinsed in CHCl3 to dissolve excess PMMA layer which may be present on the particles. Force curves of the repeatedly rinsed film are taken using an atomic force microscope (AFM) till the force curve signature of the PMMA film disappears, leaving a uniform distribution of MoS2 particles glued at the bottom by the PMMA, to the silicon substrate.

For the low load experiments, first a layer of PMMA is spin coated on the Si wafer and then the particle suspension is poured on the PMMA layer and spin coated. The sample is heated to 150 °C in an oven so that the PMMA layer melts and acts as an adhering layer for the MoS2 particles. This is done carefully to ensure that, except for a small region at the bottom, the particle remains uncovered by the PMMA.

The EN-31 and SS 304 steel were machined and ground to give sample dimensions, 15(l) × 15(b) × 5(h) mm and 25(d) × 5(h) mm respectively. The samples were then polished using 220, 320, 400, 600, 800, 1000, 1200 and 1500 grit silicon carbide papers. After polishing the samples were rinsed in acetone (AR Grade, s d fine-chem, India) and then disk polished using diamond paste of (a) grade 1–3 μm followed by (2) grade 0.5 μm. The polished samples were cleaned by ultrasonication in acetone to remove all polishing debris. The MoS2 particles were spin coated onto the steel substrate from the suspension in n-hexane and were stored in a desiccator prior to subjecting them to dry tribological characterization. For the lubricated tribology, microtribometric experiments were done by placing 25 μl of monolithic and agglomerated MoS2 particle suspension in hexadecane or water (20 mg MoS2 in 10 ml) on the steel substrate. After the tribological tests the samples were stored for further spectroscopic and microscopic characterization of the tracks created in the microtribometer.

2.3. Lateral force microscopy

Tangential traction was applied on a 1 μm × 1 μm flat portion of a particle in lateral force microscopy (LFM) using an atomic force microscope (Explorer, Thermomicroscope, Vecco, USA). The cantilever used for the high load experiments is of stiffness 42 N/m and the tip used is antimony doped Si with an end radius of 15 nm. After each LFM experiment, the topography of the particle is measured and the difference of the height from the initial peak gives the thickness of material removal. At a particular normal load, we have performed the LFM experiment 10 times to obtain the thickness of the material removed after each scan. The stiff cantilever allowed experiments to be performed to 10,000 nN normal load without either the tip and/or the cantilever being damaged. The tip was changed when an SEM (Scanning Electron Microscopy) image of the tip after an experiment was found to have changed the tip radius substantially.

Low load LFM experiments were performed using an Explorer AFM (Thermo Microscopes, Santa Barbara, U.S.A.) with Si3N4 cantilevers (Vecco, USA) that have pyramidal tips of a nominal end radius of 20 nm, under ambient condition (21 °C, relative humidity 35%–45%). A V-shaped cantilever (normal force constant, 0.15 N m⁻¹) was used to measure the normal and lateral forces. All the tips were cleaned in a UV chamber (Bioforce Nanosciences, USA) for 20 min before use. For friction force measurement, as already reported earlier [23] we considered the difference in lateral force images recorded in the forward and reverse scans, and we report here an average of this difference. The lateral force was recorded using 1 μm × 1 μm scan area.

2.3.1. AFM cantilever calibration

The normal sensor (NR) response (A/m) was recorded from the repulsive part of the force distance curve. Known the normal cantilever stiffness (N/m) from the manufacturer and the sensor response during an experiment we estimate the normal force. We used a finite element (FEM) based technique [23] to estimate the torsional or lateral stiffness of the ‘V-shaped’ Si3N4 and rectangular Si cantilevers that is used here. This method does not require a ‘multiple cantilever’ (where one cantilever is of rectangular geometry [24]), additional mass [25] or a well-defined scanning geometry (‘wedge calibration method’ [26]). Writing an angular response AR = NR × L/ϕ for the present cantilevers the FEM estimation gives T/ϕ = 1.6 × 10⁻⁹ Nm/rad for the 0.15 N/m cantilever and 5 × 10⁻⁸ Nm/rad for 42 N/m cantilever.
2.4. Microtribometer (MTR)

Microtribological experiments were carried out in the range 20–700 mN using a nanotribometer (CSM Instruments, Switzerland). The nanotribometer is composed of three stepper motors (two in X- and Y-axis linked to pin-on-disc module and one in Z-axis linked to measuring head). The cantilever was mounted on the measuring head. A 2 mm diameter steel ball (rms roughness ~1–2 nm) is attached to the end of the cantilever. Before attachment, the steel ball was cleaned in acetone using an ultrasonic bath. Two optical sensing mirrors placed near the cantilever head, perpendicular to each other (X- and Z-axis), measure the displacement of the cantilever during sliding against the substrate. The friction coefficient was determined during sliding by noting the deflection of the cantilever in both horizontal and vertical planes. All measurements were carried out in reciprocating mode under ambient conditions (relative humidity: 35–45%, temperature: 295 K).

2.5. Pin-on-disc

Macrotribological tests were carried out using a pin-on-disc machine, procured from DUCOM (Bangalore, India). The flat face of a high-speed steel pin (diameter 3 mm, rms roughness ~100 nm) was loaded normally (60 N) and pressed against the flat surface of a rotating disc (rms roughness ~400 nm). The disc was slid against the pin at 0.3 m/s surface speed. The friction force was measured by a load cell attached to the pin holder (resolution 0.1 N) and the displacement of the pin was measured using a Syscon (Bangalore, India) displacement sensor (LVDT, resolution 0.1 μm). Prior to the actual experiment a full pin-on-disc contact was established by running in; load 5 N speed 60 rpm. The disc was slid against the pin at 0.3 m/s surface speed. The friction force was measured by a load cell attached to the pin holder (resolution 0.1 N) and the displacement of the pin was measured using a Syscon (Bangalore, India) displacement sensor (LVDT, resolution 0.1 μm). Prior to the actual experiment a full pin-on-disc contact was established by running in; load 5 N speed 60 rpm. For the dry tests prior to the actual experiment a full pin-on-disc contact was established by running in; load 5 N speed 60 rpm. For the dry tests prior to the actual experiment a full pin-on-disc contact was established by running in; load 5 N speed 60 rpm.

2.6. MTR track analysis

To explore the status of the particle in the slid track of the MTR and pin-on-disc, the samples were subjected to further investigation. Microscopic features of the samples were obtained using scanning electron microscopy (FEI, Sirion). Resonance Raman spectra were recorded at room temperature using a standard backscattering geometry applied with Renishaw inVia reflex micro Raman spectrometer. Excitation wavelength of 785 nm was produced by a near IR diode laser source capable of supplying 300 mW of power. Several locations of each sample were probed to ensure reproducibility of the data. In order to prevent damage to the samples, different optical filters were used to reduce the incident power. Spectrometer was calibrated by Si line at 520 cm⁻¹.

2.7. Nanoindentation

Young’s modulus and hardness of a single MoS₂ monolithic particle and an agglomerate were determined by nanoindentation using a diamond Berkovich tip of 100 nm tip radius (Young’s modulus: 1140 GPa) in a nanoindenter (Hysitron Tribolindenter, Hysitron Inc., Minneapolis, USA). To facilitate nanoindentation of single MoS₂ particles, particles were immobilized on the silicon wafer as described above. Prior to the indentation, the sample topographical images were acquired. From the image a single particle is selected for indentation measurements. The indentation load was applied normal to the basal plane. The load was increased from 25 to 250 μN in increments of 25 μN. The load-displacement characteristic for each particle was recorded and Oliver and Pharr [27] equations were used by the built-in software to estimate the hardness and Young’s modulus.

2.8. Dynamic light scattering

The particle size distribution in HD and water suspensions was measured by 90plus nanoparticle size and zeta potential analyzer (Brookhaven Instruments, USA). The particle suspension was prepared by suspending 50 mg of monolithic and agglomerated MoS₂ particle in 100 ml of HD/water using an ultrasonic bath and an ultrasonic probe (VCX-500, 20 kHz frequency, Sonics and Materials Inc. USA). The surfactant/dispersant used for dispersing the particles are poly isobutylene succinimide (PIBS) and cetyl trimethyl ammonium bromide (CTAB) for HD and water respectively. The particle analyzer consists of a 30 mW solid-state laser for the scattering of the particles and the Photo Multiplier Tube detector to measure the scattered light at a 90° scattering angle and gives the characteristic particle size distribution and charge on the particles. The effective hydrodynamic diameter (d) of the particles in the dispersed suspension is determined using a second-order cumulant function to model the autocorrelation function and solve the Stokes–Einstein equation. A cylindrical cell of 1 cm diameter is used for the purpose and 2 ml of suspension is required to make the measurements.

3. Results

3.1. Lateral force microscopy (LFM) of single MoS₂ particle in liquid medium

Fig. 1a shows an agglomerate, of roughly the same size as the monolithic particle, to consist of many randomly oriented 50 nm crystallites. Fig. 1b shows the SEM images of a monolithic and the agglomerated state of the small particles. The agglomerate diameters are found to vary between 1 and 20 μm.

The low (10–90 nN) and high (100–10,000 nN) load coefficient of friction data were recorded using 0.15 N/m stiffness Si₃N₄ and 42 N/m Si cantilever respectively. Fig. 2a shows the coefficient of friction (10 scan average) as a function of normal load. The coefficient of friction data of the monolithic particle and the agglomerate in the ambient are reproduced from our previous work [28]. LFM scan of the particles in liquids (Fig. 2a) shows the level of friction of the particle to be reduced from that in the ambient. For the monolithic particle the coefficients of friction in water and oil are about the same in the low load regime, the value increases with normal load till the load is about 100 nN. At higher loads unlike in the case of the ambient the coefficients of friction in the liquid media decrease with increase in load, the value being higher in the water medium than in the oil. These trends continue till about 2000 nN where the monolithic particle in oil registers a very low (≤0.01) friction. At loads above 2000 nN, the friction coefficient generated in the liquid increases with load, the increase is catastrophic when the medium is oil. For the agglomerate, the medium dictated frictional differential of the monolithic particles, is maintained, the coefficient of friction increases monotonically but non-linearly till about 1000 nN (Fig. 2b) above which load all the three coefficient of friction characteristics show a decline with increase in load.

Fig. 3 shows that for the tests in the ambient the average thickness of the material removed by scanning increases with load to a level of about 40–50 nm at 2000 nN, at higher loads the thickness of the removed material does not change substantially with load. When the tests are done in the water medium, trends similar to that in the ambient is observed but the plateau is at a higher level (90 nm) than what it is in the ambient. When the medium is oil the material removal per scan increases with load to a very high level (230 nm at 1000 nN). At higher loads the wear reduces rapidly with load. With reference to Fig. 2a it is seen that this is also the load regime (3000–10000 nN) where the friction coefficient in oil increases rapidly with load to a very high value. It is possible that in the oil medium the particle fragments severely under these very high pressures.
(\sim 20 \text{ GPa})$ promoting direct contact of the sharp AFM probe with the substrate. We will show later (Fig. 6c) that even under a pressure of $\sim 12 \text{ GPa} (800 \text{ nN})$ the probe penetrates the particle leaving a residue of 200–300 nm of the particle on the substrate. It is also interesting to note that this very high pressure phenomenon does not occur for the monolithic particles in the ambient and in the water medium as well as in the case of agglomerates where the fragmentation and material removal under these pressures are much less severe (Fig. 3, 4, 6). For the agglomerate, the material removal characteristics for all the three test media are about the same (Fig. 4). At very high loads, the average
thickness of material removed per scan for the test medium is about 80 nm. Fig. 5 gives a summary of the test results at 800 nN normal load.

To rationalize the LFM tribology results, in Fig. 6 we map the particle profiles obtained with repeated scans at constant load. Broadly there are three types of material removal processes in response to a scratch in a 1 μm x 1 μm scan area.

1. A slab of material of about 10 μm length (length of the particles) and 2 μm width is removed in response to the scratch, (Fig. 6a). The thickness of the slab increases with normal load up to about 1000 nN load, it remains more or less invariant with load at the 40–50 nm thickness level in the 1000–10,000 nN range (Fig. 3a). This behavior is observed for the monolithic particle in the ambient and in the water medium (Fig. 6a and b).

2. The LFM probe makes a groove in the particle. This is seen whenever an agglomerate is scanned irrespective of the medium, Fig. 6d, e and f.

3. The traction fragments the particles, Fig. 6c. The figure shows the monolithic particles breaking up under traction in the oil medium.

3.2. Microtribometer studies of particles sprayed on a steel substrate

A lubricant was prepared by suspending MoS2 particles in oil. A drop of the suspension was sprayed on the steel substrate and...
microtribometry was done using that drop as a lubricant. The microtribometric experiment where a steel ball makes contact with a number of particles simultaneously gives in general (Fig. 7) the same trend with respect to load and medium as given by the single particle LFM experiments, except that the levels of coefficient of friction obtained in the former is somewhat higher than what is achieved in the latter. Increasing the sliding velocity lowers the coefficient of friction in all the microtribometric experiments reported here. Fig. 8 shows that the results of experiments done on a large scale (contact area), in a pin on disc (POD) apparatus, reproduce the trends of results obtained by microtribometry. What is however interesting is that the POD lubricated tests with particles dispersed in oil give roughly the same order of coefficient of friction ($\sim 0.04$) as that obtained in the LFM tests where the particles were immobilized on the substrate and the experiment was done in oil. This value of coefficient of friction is significantly lower than that ($\sim 0.07$) obtained in the lubricated sliding of the steel ball on the sprayed particles (Fig. 7).

3.3. Raman spectroscopy

There are four key first-order Raman active modes in the MoS$_2$ [29,30], designated as $E_{1g}$ (286 cm$^{-1}$), $E_{2g}$ (383 cm$^{-1}$), $A_{1g}$ (408 cm$^{-1}$)
and $E_{2g}^2 (32 \text{ cm}^{-1})$. The first three modes are due to vibration of atoms within a S–Mo–S layer. The fourth mode, $E_{2g}^2$, is associated with the vibration of a MoS$_2$ layer against neighboring layers, this is called the rigid-layer mode. In backscattering experiments on a surface perpendicular to the $c$ axis, the $E_{1g} (286 \text{ cm}^{-1})$ mode is forbidden. The observed Raman spectra (Fig. 9a) for the bulk MoS$_2$ is well matched with that observed previously [30] except the $E_{2g}^2$ mode at 32 cm$^{-1}$. The low frequency $E_{2g}^2$ mode may not have been clearly resolved by the present spectrometer with a relatively low energy laser source.

In a previous paper [31] we have shown that under conditions same as that which prevails in the present experiments, a weak Raman signal similar to the one shown here as Fig. 9d is obtained in a region of the track where there is a 80–100 nm thick monolithic MoS$_2$ transfer film. What is interesting about the data presented here is that compared to that shown in Fig. 9d higher intensity signals corresponding to Raman shifts of 186, 235, 380, 406 cm$^{-1}$ are obtained (Fig. 9b and c) when the particles are dispersed in oil. This indicates that thick anti-friction films of MoS$_2$ are formed on the substrate when the monolithic particles dispersed in oil are used as lubricants.

In contrast when sprayed monolithic particles are slid in the ambient, the tribo-film generated on the POD track does not
reproduce the bulk spectrum. Fig. 8 shows that the friction coefficient recorded in the latter experiment are significantly higher than when the tribofilm is generated using a HD suspension. Although we observed a thick deposit of material on the disc and the pin surfaces (Fig. 10), Raman spectra of the tracks generated in POD in the ambient condition (Fig. 9e) do not match with that of the pristine MoS2 spectrum. Broad peaks are seen for the films generated under ambient condition at Raman shifts of 143, 224, 290, 405 cm$^{-1}$. These peaks match with the signature of amorphous nanowires of MoS2 [32–34]. Although we did not notice any signatures of oxidized MoO2 and MoO3 at 800–1000 cm$^{-1}$ wave numbers, it is possible that the contact temperature reached in the ambient experiments is high enough to introduce defects inside the MoS2 lattice, resulting in an amorphous transfer film. As no amorphous transfer film was recorded in lubricated tribology it may be suggested that oil transfers some of the heat away from the contact.

4. Discussion

We have previously [28] explored the mechanism of deformation of single monolithic and agglomerated MoS2 particles under tangential traction. We have also stated [31] that when the tribology is done in the ambient the levels of and trends in the friction characteristics of these particles sprayed on a steel substrate can be explained with the help of understandings arrived at from the single particle work.

Major practical applications which involve these particles are however in the field of lubricated tribology. The most interesting result to emerge from the present work is that in a certain range of nominal constant pressure and sliding velocity it is possible to obtain a very low (≤0.01) coefficient of friction by dispersing the large monolithic MoS2 particles in oil and this value of the coefficient of friction is about two orders lower than what is achieved in the ambient. We suggest below a model, which attempts to explain why this happens and provide supplementary data to examine its validity. When an experiment is done in oil, the oil is ingested by the highly lipophilic particle such that the oil is absorbed homogeneously throughout the particle. This weakens the particle such that even under modest loading the particle fragments into smaller units. Small particles have good access to the contact zone and participates in generating a good and stable antifriction transfer film.

Fig. 6c shows that a monolithic MoS2 particle fragments in oil medium in the LFM under a 800 nN load. Fig. 11 shows the ingestion of liquid by a monolithic particle. The oil is ingested easily by the particle. In comparison, the ingestion of water by the particle in the same time frame is very small. Measurement of contact angle of water and oil droplet on MoS2 surface gives 90° and 0° contact angles, respectively, indicating that MoS2 is principally hydrophobic and is well wetted by oil.

Nanoindentation tests on single particles of MoS2 gave Young’s moduli in the 20–30 GPa range for the monolithic particles and 5–10 GPa for the agglomerate. The recorded moduli correspond well with those reported by others [35,36]. However when the tests were done in a HD medium, the corresponding Young’s moduli are in the range of 5–6 GPa for both the monolithic and agglomerate particle. MoS2 is a highly anisotropic material. The planar (basal plane) modulus of a monolayer is high of the order of 240–250 GPa. We record here the modulus in a direction normal to the basal plane. The hardness values recorded in the ambient are ~0.6 GPa and ~0.2 GPa for the monolithic particle and agglomerate respectively. In the HD medium the hardness values for both the particles are found to be similar and in the range of 0.2–0.3 GPa. It is likely that the low modulus and hardness we report for the agglomerates are not intrinsic bulk properties of the particles but reflect a composite response of the particle/particle interface and that of the bulk material.

The implications of these results are

(1) increasing the normal load may enhance particle fragmentation, and
(2) if the particles do not ingest the liquid well and as a result are not well fragmented under load, as it would happen in a non wetting liquid medium, their transfer to the active contact zone may not be very efficient. Thus if the coefficient of friction is related directly to the particle size the above would suggest that the coefficient of friction should decrease with increasing load and the friction coefficients in the ambient and in the water medium are necessarily higher than that achieved when the lubricant liquid is oil. These effects of external parameters on friction are seen in Figs. 2a and 7.

4.1. Tribology of sonicated particle suspensions: monolithic MoS2

To take the discussion one step further we sonicated the MoS2 particles in oil and water using dispersants PIBS and CTAB respectively to control their size and dispersion prior to the suspension being used.
**Fig. 12.** Particle size distribution of the monolithic MoS$_2$ particles suspended in (a) HD and (b) water; (c) with 1 mM dispersant, PIBS (in HD) and CTAB (in water); (d) suspension mixed using an ultrasonic probe.

**Fig. 13.** Coefficient of friction from MTR studies of the monolithic MoS$_2$ particles (a) suspended in HD and water; (b) with 1 mM dispersant, PIBS (in HD) and CTAB (in water); (c) suspension mixed using an ultrasonic probe. Sliding speed: 0.02 and 0.5 cm/s. The effective particle diameter ($\sigma$, given by the DLS software) is given for each stage (top-water and bottom-HD).
as a lubricant in tribology. Fig. 12 shows that it is possible to achieve very small particles (112–114 nm) sonicating a suspension of monolithic MoS$_2$, dispersed in oil by PIBS. A similar procedure using the dispersant CTAB in water gives particles of 275–278 nm size.

Comparing Fig. 13 with Fig. 7 it is clear that the coefficient of friction of the oil suspension is not seriously affected by sonication and dispersion. This implies that just the ingestion of oil by the particle takes the particle to a physical state where application of traction fragments it to a size of 110–180 nm (Fig. 12), and this simple process is good enough to ensure low friction. The situation is a bit different when the scratching is done in water. Fig. 6b shows that the particle is fragmented only partially when scratched in water. Fig. 12 however shows that it is possible to further the process of fragmentation by artificial agitation using a CTAB dispersant. Fig. 13 shows that apriori reduction of particle size from 1300 to 350 nm by agitation lowers the coefficient of friction from 0.2–0.4 to 0.12–0.15. These numbers are clearly greater than what is achievable in an oil lubricated experiment using 110 nm particles. We suggest that this difference may be attributed to particle size and/or to the fact that the carrier water on its own registers a higher friction than oil as seen in Fig. 8.

Another interesting observation one may make from Fig. 13 is that the large difference in friction observed between the high speed and low speed experiments in water is reduced as the apriori particle size is reduced from 1300 nm to 280 nm. This difference is also reduced further with increasing load. In a previous paper [31] on ambient ball-on-flat tribology of sprayed MoS$_2$ particles we had observed that during sliding the small particles have a tendency to move away from the center of the contact towards the edge of the track. We have argued that as at high speed the particles do not have sufficient time...
to move away in between successive contacts. They are therefore captured by the contact. The friction in high speed sliding is therefore low compared to what is achieved at low speed. At low speed the particles have enough time in between successive contacts to move away from the contact resulting in metal to metal contact and high friction. When the experiment is done in a liquid medium the liquid drag may prevent such a free mobility of the particles. In Fig. 13a the particle size is 1300 nm. For a given sliding time the average number of contacts such a particle is subject to, at 0.5 cm/s sliding speed, is 25 times more than the number it is subject to when the speed is 0.02 cm/s. We suggest that particle fragmentation increases with increasing number of contact. Further increasing the normal load also increases fragmentation. If we take these mechanisms together, then using the model we propose in the paper that smaller particles have greater access to contact in reducing friction we may expect a converging trend in friction between the two velocity characteristics as seen in Fig. 13 a and b. As the particle gets smaller they possibly become more difficult to fragment and we see two overlapping velocity characteristics in Fig. 13c.

4.2. Agglomerated MoS₂

The effect of artificial sonication, fragmentation and dispersion is even more dramatic when 50 nm particles are agglomerated. Fig. 14 gives the effect of sonication on the size of the agglomerate. Unlike in the case of the monolithic particle, the agglomerate when sonicated for 10 minutes in oil without any dispersant do not fragment substantially. The friction coefficient at low speeds (Fig. 15a) then remains high.

Gentle sonication of an oil suspension of monolithic particles reduces the average size from 2000 nm to 180 nm, while the same treatment of a suspension of 2000 nm agglomerates yields a size of 900 nm. Fig. 11 does show that oil is ingested somewhat less by the agglomerate (e.g. 0.45 gm² at 400 s) than it is by the monolithic particle (0.75 gm² at 400 s). If a low level of ingestion of the oil by the agglomerate is indeed the reason for the large size of the sonicated particles why is it difficult to fragment it by gentle sonication? We are not very clear at this stage as to why the ingestion is low in the case of the agglomerates. Agglomerates consist of defect free 50–60 nm crystallites with well-defined grain boundaries. Physical forces keep these crystallites together creating spatial mismatch defects at the boundaries. The oil permeates into the defects and voids in such boundaries. The data given here would suggest that the process of manufacture of large monolithic particles introduce a higher level of defect density in the monolithic particles than what is accommodated at the grain boundaries of an agglomerate. Sonication and ultrasonication with appropriate dispersant in oil reduces the particle size and the corresponding friction coefficient substantially (Fig. 15 b, c). It is interesting to note that the friction coefficient, even after severe agitation in oil with an appropriate dispersant is never reduced to the same level as that achieved with monolithic particles (Fig. 13) although the particle size achieved with the agglomerates is smaller than that achieved with the monolithic particles. We are inclined to suggest that not all the crystallites, sonicated out of the agglomerates, reach the contact zone with their basal plane favorably oriented. At present we have no suitable explanation as to why this happens.

Comparing Figs. 13 and 15 it is also clear that great benefits accrue with even a gentle sonication of monolithic MoS₂ in oil without a dispersant (Fig. 8). Such benefits are not achieved when the precursor particles are agglomerates as well as when the medium is water. For both the latter cases vigorous sonication and dispersion need to be undertaken to reduce the particle size and generate low friction tribological conditions.

5. Conclusions

The results we present here indicates that it is the natural tendency of oil to wet and permeate into the bulk of a monolithic MoS₂ crystal which makes the difference between the tribological performances of MoS₂ crystal suspended oil lubricant and those made with agglomerates and water. The ingestion of oil weakens the particles and fragments them to sizes which allow easy transport of particles to the contact zone, formation of robust antifriction films at the interface and low friction tribology. To achieve the latter with agglomerates and water medium, significant agitation of the suspension need to be done with suitable dispersants.

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