On the matter of Synovial Fluid Lubrication: Implications for Metal-on-Metal Hip Tribology

Connor Myant and Philippa Cann, Tribology Group, Imperial College London, UK

Corresponding author: connor.myant@imperial.ac.uk

ABSTRACT

Artificial articular joints present an interesting, and difficult, tribological problem. These bearing contacts undergo complex transient loading and multi axes kinematic cycles, over extremely long periods of time (>10yrs). Despite extensive research wear of the bearing surfaces, particularly metal-metal hips, remains a major problem. Comparatively little is known about the prevailing lubrication mechanism in artificial joints which is a serious gap in our knowledge as this determines film formation and hence wear. In this paper we review the accepted lubrication models for artificial hips and present a new concept to explain film formation with synovial fluid. This model, recently proposed by the authors, suggests that interfacial film formation is determined by rheological changes local to the contact and is driven by aggregation of synovial fluid proteins. The implications of this new mechanism for the tribological performance of new implant designs and the effect of patient synovial fluid properties are discussed.

Key Words: metal-on-metal hips, artificial joints, film thickness, wear, bovine serum, synovial fluid

NOMENCLATURE

BCS	Bovine calf serum
CrCoMo	FS75 chromium, cobalt and molybdenum alloy
CoC	Ceramic-on-Ceramic
EHL	Elastohydrodynamic lubrication
LHMoM	Large Head Metal-on-Metal
MoM	Metal-on-Metal
MoP	Metal-on-Polymer
OA	Osteoarthritis
PAL	Protein aggregation lubrication
s	Inlet reservoir length
SAPL	Surface active phospholipid
SF	Synovial fluid
Ra	Arithmetic mean surface roughness
R'	reduced radius
U	Entrainment speed
W	Applied load
η	Dynamic viscosity

1 **Introduction**

Prosthetic implants restore joint function which has been impaired due to disease, trauma or genetic condition. Due to an ageing population this is a rapidly growing sector; National Joint Registry (2012) figures for England and Wales reported 88,984 total hip and 93,080 knee replacement procedures in 2012. However, there are significant clinical concerns over the use of 2nd generation Metal-on-Metal (MoM) hip joints as these have been associated with the development of periprosthetic tissue lesions (Revell *et al*., 1997). These concerns resulted in the issue of a medical device alerts by the UK MHRA (2010) for MoM implants and the withdrawal of some designs from the market.

MoM hips are not a recent concept; they were first introduced in the early 1960s with the McKee-Farrar cemented joint, which used a CoCrMo alloy for the head and articular cup. Although these were widely implanted, early failures did occur due to asceptic loosening and poor manufacturing quality. As a result the implant was discontinued in favour of the Charnley Metal-on-Polymer (MoP) hip. However, for some patients the McKee-Farrar joint had good survivorship (> 20 years) with no apparent attendant problems (Isaac *et al*., 2006). In the late 1980s attention turned again to the MoM design as a replacement for MoP hips, which were found unsuitable as a long term solution for younger patients. The second generation MoM designs, which included resurfacing, larger head diameters (LHMoM) and modular hips, were driven partly by clinical requirements of reduced risk of dislocation, ease of implantation, conservation of bone stock and greater degree of movement. Although the hip simulator studies indicated reduced wear with the large head MoM designs (Dowson et *al*., 2004; Isaac *et al*., 2006) the *in vivo* experience has been less positive. The UK NJR (2012) reports higher than expected revision rates for LHMoM joints, > 5%, compared to 2% for conventional MoM hips. Implant failure can be due to a number of reasons (NJR, 2012) including aseptic loosening, infection and breakage; however a significant number of patients experience “unexplained pain” and this is often linked to high levels of metal ions in the blood. Explant analysis has shown these hips often have high levels of wear, often due to edge-wear of the cup (Underwood *et al*., 2012). The reasons for increased wear and failure are complex and include design, metallurgy, implantation (particularly cup position) and patient factors. The patient factors include gait (Bowsher, *et al.*, 2006), lifestyle (Brown and Clarke, 2006; Shetty and Villar, 2006) and synovial fluid (SF) composition (Klein, 2006; Liao, *et al.*, 1999; Maskiewicz, et al., 2010). Excessive implant wear is essentially due to the breakdown of the lubricating film which separates the surfaces; the formation mechanisms and properties of the lubricating films are the focus of this paper.

2 Why is the lubrication mechanism important?

In many cases both short and long term failure of artificial joints is due to wear of the articulating surfaces. Material loss and damage of the surfaces may originate in physical (abrasion or adherence) or chemical (corrosion) mechanisms. These result in the formation of micron (polymer) or nanometre (metal) sized wear debris which is biologically active and often provokes an adverse cellular response (Wroblewski *et al*., 1993, Hart *et al*., 2006, Revell *et al*., 1997). The development of wear-resistant materials, including cross-linked polyethylene (Wang *et al*. 1998), metal treatment (Varano *et al*., 2006) and ceramics (Essner *et al*., 2005) has been the focus of much research over the years (Katti *et al*., 2004). However the range of materials available to the implant designer is limited as these must be low wearing, biocompatible; both in bulk and particulate and easy to manufacture to a reliable standard (Katti *et al*., 2004).

The other approach to improving wear performance is to optimise the lubrication function of the joint, to exploit this we need to understand the film formation mechanisms occurring during articulation. Currently there are two general theories; fluid film EHL (Dowson, 2006a) and boundary lubrication (Hills, 2000) mechanisms. Although these theories are often treated separately it is highly likely, depending on the implant operating conditions, both will contribute to lubricant film formation during articulation.

Most tribology studies of implants have focussed on the measurement of wear; either in simple pin-on-disc devices to study fundamental material properties (Tipper *et al*., 1999; Yao *et al*., 2003) or in more complex hip simulators where the effect of additional implant parameters (design, gait, position) can be assessed (Bowsher *et al*., 2009; Fisher *et al*., 2004; Medley *et al*., 1997). Wear is essentially determined by the lubricant film and material properties. It is, therefore, important to understand lubricant behaviour over the entire gait cycle; including film thickness and distribution in the loaded-contact zone. Artificial joints undergo a range of loading and kinematic conditions during operation. The kinematics are complex as the load, sliding speed and direction of sliding all change within the cycle. Identifying the lubrication mechanism (or mechanisms) operating over the gait cycle will provide the most reliable basis for predicting wear and provide the underpinning knowledge necessary to optimise implant and material development.

3 Stribeck analysis of lubricated contacts

The likelihood of surface damage is often represented in a Stribeck curve (Stachowiak and Batchelor, 2005) which relates friction coefficient and wear as a function of a duty parameter; $U\eta/W$. Where U is the entrainment speed, η the dynamic viscosity and W the applied load. A representative diagram of a Stribeck curve is shown in Figure 1a. Whilst Figure 1b presents a representative sketch of the contact, indicating the location of the main contact, inlet and exit regions. Lubricant film formation is generally described as a result of chemical (Boundary Lubrication) or fluid flow effects (Hydrodynamic or Elastohydrodynamic lubrication). The “boundary”, “mixed” and “hydrodynamic” lubrication regimes are indicated on the Stribeck curve. The contribution of these mechanisms to total film thickness will depend on the lubricant properties and operating parameters. The hydrodynamic mechanisms rely on the relative movement of the surfaces to entrain fluid into the contact zone and form a separating film; this mechanism will predominate at high speeds and for high fluid viscosities.

At low duty parameter values a separating (load bearing) fluid film is not formed, this is known as the boundary regime. Friction coefficient and wear are high due to large plastic deformation of surface asperities. This behaviour can be modified in the presence of boundary additives, as indicated in Figure 1a. Film formation is determined by chemical rather than physical (viscosity) properties, as the boundary layer can be formed by either chemical reaction, chemisorption or physisorption mechanisms (Stachowiak and Batchelor, 2005). Typical boundary additives have polar or reactive chemical bonds which interact with the metal surface to form a coherent, low-shear stress film which resists asperity penetration and reduces friction and abrasive/mechanical wear. As the duty parameter increases the fluid film thickness also increases gradually separating the contacting surfaces. The friction coefficient drops due to a reduction in asperity interaction, reaching a minimum before increasing again. This decreasing regime is known as the “mixed” regime, friction arises from both surface interactions and fluid forces. The increase in friction at high duty parameter values is due to the increasing film thickness and thus a greater fluid shear contribution to the measured friction. Once a separating film is formed wear due to adhesive/mechanical wear ceases; any continuation is due to debris (third body abrasion) and chemical (corrosive) components within the lubricant.

The onset of the different lubrication regimes is often identified by the λ ratio, defined by equation (1); it represents the ratio between surface separation and composite surface roughness of solid bearings;

$$\lambda = \frac{h_{min}}{\left(Ra_1^2 + Ra_2^2\right)^{1/2}} \tag{1}$$

where h_{min} is the minimum film thickness and Ra the surface roughness of the respective contacting bodies. Figure 1a presents a typical Stribeck curve of friction coefficient *versus* contact parameters with the λ ratios for different lubrication regimes indicated. These are;

λ>3 Fluid film regime: the surfaces are fully separated and mechanical wear is minimised

λ = 1-3 Mixed lubrication regime: intermittent contact of surface asperities with some wear and fluctuating friction coefficient

λ<1 Boundary regime: the surfaces are in close contact often with high friction coefficient and significant wear.

However it must be remembered that the Stribeck curve, and lambda ratio, were developed for journal bearings lubricated by simple hydrocarbon oils under steady-state loads and speeds. The applicability of such a simple analysis to the more complex case of implant lubrication undergoing transient loads and speeds with a multiphase fluid is questionable.

4 Tribological conditions in artificial joints

One of the problems encountered when considering implant lubrication is the complexity of the system. The hip joint experiences transient loading and variable sliding velocities over the gait cycle, which results in a range of contact conditions and possible lubrication mechanisms. Typically these joints function at slow speeds, low pressures and transient loading under reciprocating sliding. For example in steady-state walking, replacement hip joints, experience two loading peaks per cycle with loads varying from ~0.1 to 3.5 KN and linear speeds of 0-30 mm/s. The maximum contact pressures are generally low (<70 MPa), compared to engineering contacts. However, physiological kinematics and loads can vary markedly for different activities and patients (Bergmann *et al*., 2010).

The other part of the problem is the lubricant, which is periprosthetic synovial fluid (SF). SF is a complex mixture of macromolecules (protein, glycoproteins, hyaluronin) and surface active species (phospholipids) (Kitano *et al*., 2001; Wang *et al*., 2003). The chemical composition includes hyaluronan (HA), proteins and glycoproteins, phospholipids and cholesterol (Kitano *et al*., 2001). A number of these species, particularly phospholipids and proteins, are thought to contribute to the boundary lubrication of the implant. The problem is further complicated by changes to the physical and chemical properties of SF due to disease, trauma and postoperatively (Kitano *et al*., 2001; Wang *et al*., 2003; Delecrin *et al*., 1994), so that there is no "typical" composition. Periprosthetic SF, which refills the cavity post-implant, has different properties to healthy SF; the pH and protein concentrations increase and the effective viscosity decreases due to changes in the HA content (Kitano *et al*., 2001; Delecrin *et al*., 1994). The major chemical constituents and physical properties of SF are summarised in Table 1.

The rheology of SF is complex as it is rheopectic at low (<10^0 s^{-1}) (Oates *et al*., 2006) and shear-thinning at high shear rates (Cooke *et al*. 1978). Rheopexy is defined as an increasing stress as a function of time at a constant shear rate. At low shear rates protein molecules are reported to aggregate forming a three-dimensional network, which breaks down at high shear rates (non-Newtonian behaviour) (Oates *et al*., 2006). Measured viscosity for healthy SF at assumed physiological shear rates (> 10^3 s^{-1}) is typically in the range 0.01-0.1 Pas (Cooke *et al*. 1978). For diseased and post-arthoplasty SF the high shear rate viscosity drops to less than 0.001 Pas (Cooke *et al*. 1978). For SF it is usual to assume that at physiological shear rates the effective viscosity is constant (2nd Newtonian regime). Typically a value of 0.002-0.005 Pas is used in film thickness modelling calculations (Wang *et al*., 2008).

25% BCS has been commonly employed as the model screening fluid for healthy SF; the solution has a similar total protein concentration and non-Newtonian rheology (Cooke *et al*., 1978). Recently, the ISO standard governing the preparation of screening fluids for hip joint simulators altered the dilution of BCS from 25% ± 2% (Kaddick and Wimmer, 2001) to 30 ± 2 g/l (ISO #14242-1, 2012) or *ca* 50%. This reflects the increased protein concentration observed for periprosthetic SF. However, the standard does not provide protocol for additional components; for example there are differences in the ratio of proteins (albumin and γ-globulin) and phospholipid content. BCS also lacks other important components; such as hyaluronan. The development of a more pertinent screening fluid will require a fundamental understanding of the lubrication mechanisms controlling implant wear and the effect of patient SF composition.

5 Conventional lubrication models in artificial hips

Two very different classical lubrication mechanisms have been proposed for MoM joints these are boundary (Hills, 2000; Gale *et al*., 2007; Roba *et al*., 2009; Wang *et al*., 1998) and EHL (Dowson and Jin, 2006b; Jalali-Vahid *et al*., 2006; Jin, 2006).

5.1 Boundary lubrication

Boundary lubrication dominates under conditions where a fluid film is not formed (by hydrodynamic action); these are high loads, low speeds and low fluid viscosity. A number of SF species have been identified as potential boundary lubricants; these include HA, proteins, glycoproteins and phospholipids (Gale *et al*., 2007). HA is a high molecular weight (105-106 Da) linear polysaccharide and in diseased SF the concentration and molecular weight of HA are decreased. HA is thought to contribute to viscoelasticity and viscosity enhancement (Swann *et al*., 1974) but to have negligible boundary lubrication function (Tadmor *et al*., 2003). Phospholipids are a major component of biological membranes, which form structured mono and bilayers at interfaces (Hills and Butler 1985). A major class are the zwitterionic phosphatidylcholines which have a positively charged quaternary ammonium ion (polar head) and adjacent phosphate ion. The positively-charged head group adsorbs at surfaces to form an oligolamellar layer (Swann and Radin 1972) with the long hydrocarbon chains forming a hydrophobic surface.

Other SF components have been identified as having boundary lubrication capabilities. In the late 1970s attention turned to lubricin, a highly purified glycoprotein fraction of SF as the primary boundary lubricant of articular cartilage (Swann and Radin 1972; Swann *et al*., 1981; Schwarz and Hills 1998). Analysis of lubricin indicated it contains protein and carbohydrate with a small percentage (~12%) of phospholipid. The phospholipid fraction (SAPL) was identified as the primary boundary lubricant in lubricin (Gale *et al*., 2007; Schwarz and Hills 1998). The water-soluble glycoprotein component is thought to act as a carrier for the insoluble phospholipid.

Surface analysis of explanted joints from hip simulator and retrieval studies has been reported by Wimmer *et al*. (2003). In this study surface layer formation on forty-two retrieved MoM hip joints was compared to results from in vitro test specimens. The paper reported evidence of thick carbon-rich deposited layers on over 80% of the components. These films were usually "within or at the border of the formerly articulating surfaces". They concluded the films were formed by denatured proteins deposited from solution in the high pressure contact regions. It was suggested the proteins acted as a solid lubricant reducing adhesion and abrasion. There is supporting evidence from Wang and co-workers (1998) for this idea; they concluded that the protein layer acts as a "solid" boundary layer which prevents adhesive wear. Examples of thick deposited films on an explanted joint are shown in Figure 2a; the "rainbow" colours indicate film thickness in the range 200-500 nm. FTIR reflection-absorption analysis of the film on the explanted head showed it to be protein-based with significant γ-globulin content (Burgett et al., 2013). Deposited films formed on the stationary surface used in a reciprocating test are shown in Figure 2b, again the rainbow colours indicate thick protein films at either end of the wear track.

Organic reacted or deposited layers also appear to play a role in conditioning the alloy subsurface and thus affecting wear. Recent studies of the CrCoMo alloy published by Pourzal *et al*. (2009a; 2009b) have analysed the microstructural changes that occur in the subsurface region of retrieved (resurfacing) and simulator-tested tested MoM implants. The hip-simulator test samples indicated the formation of a carbon-rich nanocrystalline layer approximately 200 nm thick (Pourzal *et al*., 2009b). The formation of this layer through mechanical mixing (Rigney 2000) is reported to be the origin of the excellent wear resistance of the CrCoMo alloy (Pourzal *et al*., 2009a).

A few studies have analysed bulk fluid remaining in the simulator test chamber to obtain insights into lubrication mechanism (Maskiewicz *et al*., 2010). BCS solution rapidly forms precipitates during the test (Wang *et al*., 2003) and must be regularly replaced. In a recent paper Maskiewicz and co-workers (Maskiewicz *et al*., 2010) analysed protein degradation products formed during simulator tests of serum-based lubricants. They reported the formation of “high molecular weight aggregates which precipitated out of solution”. There was no evidence of protein molecular fragmentation. The major conclusion from this work was that high shear rates within the articulating interface were responsible for protein agglomeration. Other studies; for example Lu and McKellop (1997) suggested that high local contact pressures and increased temperatures lead to denaturing and precipitation of proteins.

Few numerical models exist for the boundary lubrication regime due to the complexity of coupling the contact mechanics, lubricant flow and surfactant properties. This, in part, has led to dependency on numerical simulations of film formation in artificial joints using EHL models, which are discussed in the following section.

5.2 'Fluid film' lubrication

The alternative theory is that MoM hip joints operate in the “fluid-film” regime where the rubbing surfaces are separated by ElastoHydrodynamic lubricant (EHL) film (Dowson and Jin, 2006b; Jalali-Vahid *et al*., 2006; Jin, 2006). In EHL the film formation mechanisms are very different to boundary lubrication. Friction is now a result of fluid forces (lubricant rheological properties) and not surface asperity interaction. EHL requires the entrainment of a viscous fluid which combined with the deformation of the surfaces contributes to the development of a separating film. Wear is, now, caused by chemical corrosion or 3rd body abrasion and not mechanical wear mechanisms between the main contacting bodies. For simple hydrocarbon oils the film thickness can be accurately predicted for different load and speed conditions and this has been verified by many experimental studies using optical interferometry (Spikes, 1999).

Typically EHL film thickness, *h*, is predicted simply as:

$$h \approx (\text{speed})^{n} \times (\text{viscosity})^{y} \times \text{load}^{-m}$$

However conventional EHL film thickness equations are only applicable to systems where there is a significant increase in the lubricant viscosity due to high contact pressure (Spikes, 1999). SF and BCS are aqueous suspensions and the bulk (water) rheology is typically employed when predicting contact film thickness. The viscosity of water is low, but more importantly the pressure viscosity coefficient is tiny. Isoviscous EHL equations have been developed to predict film thickness for such fluids. Hooke (1980) provides the following central film thickness equation for elastic-isoviscous (low pressure, hard) contacts;

$$h = 4.18 \frac{(U\eta)^{0.6} R'^{0.67}}{W^{0.13} E'^{0.47}} \quad (2)$$

where E' is the reduced Young's modulus defined by $2/E' = (1 - v_1^2)/E_1 + (1 - v_2^2)/E_2$, respectively, where R_{x1}, R_{x2}, E_1, E_2, v_1, and v_2 denote the radii in the entrainment direction, the Young's moduli, and the Poisson's ratios of the two contacting bodies.

EHL film thickness increases with speed (~$U^{0.6}$) but is relatively insensitive to load (~$W^{0.13}$); typically a 10x increase in load halves the film thickness. The effect of mean speed on calculated film thickness from Eq. 2 is shown in Figure 3 for simple low viscosity (0.001, 0.005 and 0.01 Pa s) fluids.

Due to the transient loads and speeds experienced over the hip gait cycle it would be expected that the predicted EHL film thickness also fluctuates, an example from Jalali-Vahid *et al*. (2006) is shown in Figure 4. Central and minimum film thickness is plotted against time over a model gait cycle for a model fluid (viscosity 0.9 mPas). Over the gait cycle central film thickness is predicted to fluctuate between 20 and 40 nm, where film formation is considered due to a mixture of hydrodynamic (entrainment speed) and squeeze film effects. Jalali-Vahid *et al.* (2006) predict that for a typical MOM hip implant with an average surface roughness of 0.01 um, a λ ratio of 1-2 is achieved, suggesting that the contact operates just within the mixed regime. The analysis also confirms the chemical (boundary) properties of the SF rather than the bulk viscosity will play an important role in determining wear.

The EHL models consider film formation to depend solely on the synovial fluid bulk viscosity (usually the assumed 2nd Newtonian value) and the operating conditions (speed, contact pressure) of the joint. The equations are used to calculate film thickness over the gait cycle and provide a relatively simple method of exploring the effects of implant parameters (kinematics, load, implant geometry) on fluid-film lubrication and thus by inference prosthesis wear. It must be remembered that such predictions are only valid if the underlying mechanisms of film formation and relationship to sliding speed and load are correct. However the correlation of theory and experiment is only verified by experimental work for simple, single phase lubricants undergoing steady-state shear and loading. For a complex lubricant containing different phases, for example an emulsion or grease (Lubrecht, 2001), the film thickness response to changing contact conditions is often very different and cannot be predicted by classical EHL models.

One of the most important factors determining film thickness is the viscosity of the fluid in the inlet region (Figure 1b) as it is this material which is entrained into the contact zone. Generally, this material is assumed to have the same composition and properties, particularly viscosity, as the bulk solution. In EHL models SF is considered to be a single phase fluid which has a Newtonian rheology at physiological shear rates (Dowson and Jin, 2006b). However SF exhibits complex rheological behaviour depending on the shear conditions (Oates, 2006). The EHL models implicitly ignore the contribution of boundary films to the lubrication process and the effect of different SF chemical composition on film formation.

5.3 Protein-Aggregation Lubrication (PAL)

The role of proteins in the lubrication process has been the focus of recent research in our group (Fan *et al*., 2011; Mavraki and Cann, 2011; Myant *et al*., 2012). Lubricant film thickness has been measured for a CoCrMo femoral head loaded and sliding against a coated (Chromium overlaid by silica) glass disc. The contact pressures and sliding speeds match those occurring in MoM hip joint. Various protein-containing lubricants were used including 25% BCS and albumin/globulin solutions. The tests used an optical interferometric method to measure the central film thickness and to follow the growth of the contact zone as the metal surface wears (Myant *et al*., 2012). Film thickness was usually measured with increasing and then decreasing speed. The results showed that film formation did not follow the classical EHL rules for a simple fluid. An example is shown in Figure 5 which plots film thickness against speed for 25% w/w BCS solution, predicted results (Eq. 2) for a fluid with a bulk viscosity of 0.01 Pa s are also shown. Typically film thickness was time dependent and tended to give much thicker films at low speeds than predicted by EHL models although this depended on the protein content (Myant *et al*., 2012). The reason for the very different behaviour observed with these fluids is the properties in the inlet region.

The model SF solutions were observed to undergo phase changes local to the contact, shown in Figure 6. The inlet zone to the contact (which is approximately 300 μm in diameter) is at the bottom of the image. The protein- aggregate is seen at the lower edge of the contact zone; the boundary has been outlined for clarity. The presence of protein-aggregate ensures much thicker films upstream in the contact zone. The rate and extent of these changes was dependent upon contact conditions (entrainment speed, load, geometry), and suspension composition (protein type and concentration). Suspended proteins collected in the inlet, which dramatically altered the lubricant composition before it entered the contact. For uni-directional sliding surface deposits were observed on the stationary component around the contact, with the highest concentration within the contact inlet zone (Myant *et al*., 2012). In bi-directional reciprocating tests depositions occurred at each end of the stroke as seen in Figure 2b. Post-test FTIR Reflection-Absorption Spectroscopy (Burgett et al., 2013) analysis of these deposits confirmed they were proteins. This inlet aggregation mechanism created a new phase with greatly increased protein content and viscosity, which is entrained into the contact generating larger than predicted films. The subsequent film distribution across the contact zone is chaotic and can vary in thickness by as much as 80 nm.

Even under steady state conditions (constant load and speed) film thickness appears transient; in time and across the contact. This is, in part, due to the seemingly random breakup of inlet aggregates as they are dragged into the contact. The dominant factor determining the level of film formation is the protein aggregation in the inlet region; thus we have adopted the PAL (Protein Aggregation Lubrication) acronym identifying this process.

For proteins, or any suspended particulate, entry to the contact will depend upon surface drag forces between the main contacting bodies and the suspended material, and their positioning relative to the central flow line (Dwyer-Joyce, 1999). On approaching the inlet zone, most of the proteins will be subject to off-axis fluid forces as the majority of lubricant flows around the contact, not through it. Thus only proteins very close to the central flow line will enter the contact. The closer the protein molecule is to the central flow line the greater the probability for contact entry. A sketch of the flow lines around a point contact, similar to an artificial hip implant, is shown in Figure 7. Entrainment speed plays a significant role in this; at low entrainment speeds, and therefore low fluid flow forces, surface drag forces dominate pulling aggregates into the contact. As entrainment speed increases the particulate are more likely to flow around the contact, due to an increase in the hydrodynamic forces flowing around the contact. This results in a decrease in film thickness and thus an inverse proportionality with entrainment speed - the opposite of classical EHL theory (Eq. 2) as shown in Figure 5. Figure 8 shows two optical interference images between a CoCr ball and glass flat, lubricated with 25%BCS. The LHS image shows the contact at low entrainment speed, RHS at high entrainment speed. Fluid flows top-to-bottom in both images. At low entrainment speeds (LHS) a large inlet is formed as off-axis hydrodynamic forces are negligible. At high entrainment speeds (RHS) the inlet length is reduced, due to the increased hydrodynamic forces the suspended proteins preferentially flow around the contact edges.

This decrease in film thickness has been related to shear thinning behaviour of the lubricant, but it can also be seen as a reduction in protein- aggregate entry to the contact. At higher entrainment speeds the lubricant in the contact is returning to bulk phase properties, although entrainment speeds far greater than those suggested for an average gait cycle are required for this to be completed (Myant and Cann, 2013).

Thick films were observed to form rapidly at low speeds after the commencement of sliding. Film thickness was highly sensitive to load and exhibited elastic properties as it recovered substantially when un-loaded, which is thought to be a result of porous networks which form within the contact. In the fluid environment the protein films are highly viscous however once removed and dried they adhere strongly to the CoCrMo surface, similar behaviour has been reported by other studies (Wimmer *et al*., 2003). In earlier papers the formation of thick deposited organic films observed on explants was ascribed to denaturing of proteins due to thermal effects (Wimmer *et al*., 2003). We agree that thermal effects could contribute to this process but we also consider that shearing will also help to form such protein aggregates and such explant studies provide further support for our model.

Clearly we need to understand in more detail the tribological role of deposited protein layers and the effect of implant (transient speed, loads) and patient (gait, synovial fluid chemistry) factors on film formation. Film formation depends on the build-up of viscous material in the inlet as such it is time-dependent and sensitive to changes in the direction of sliding. In earlier papers (Myant *et al*., 2012) the focus was on steady-state behaviour which is not representative of implant kinematics. Disruption of the inlet reservoir either by changing sliding direction, transient speeds or the passage of surface scratches, examples are shown in Figure 2a, will occur *in vivo*.

6 Implications of the PAL mechanism for implant tribology

The classical film formation mechanisms reviewed in this paper are derived from early studies with hydrocarbon fluids and simple additive systems. When applied to SF lubrication they are usually considered to be mutually exclusive with the chemists favouring boundary lubrication and the engineers EHL-based mechanisms. However, we consider both the classical mechanisms to be too simplistic as they do not address the central problem of a complex, biphasic fluid undergoing transient loading and motion. It is likely that all three lubrication regimes are experienced during a single gait cycle. The imperative to categorise SF lubrication as either "boundary" or "EHL" has been driven in part by the modelling community where the predictive models for Newtonian fluids are well-established. The assumptions implicit in the EHL models – for example film thickness increasing with speed and being relatively insensitive to load are not necessarily true for complex fluids. Any implant design based on these considerations could be fatally flawed. A possible example of this are LHMoM hips. The design of these was based, in part, on the assumption that an artificial hip predominately operates in the EHL regime during the gait cycle. And, that by following the classical EHL theorems the λ ratio could be increased (Figure 9) by simple changes to the implant design (Tipper et al., 2005). The danger occurs when full film lubrication is not achieved and the surfaces touch; the ultra-smooth surfaces and highly conformal contact create a large real area of contact. This creates seizure or scuffing like conditions which will cause high levels of wear. The drive to improve bearing performance by only increasing λ is too simplistic (Cann, et al., 1994). Many of the new generation artificial hips based on this principle are now experiencing high revision rates (National Joint Registry, 2012) and in some cases have been recalled from the market (MHRA, 2010). It has been known for many years, within other tribology lead industries, that other surface topography parameters, which are not employed in Eq. (1), also determine wear performance and bearing life (Hirst and Hollander, 1974).

It is difficult to derive fundamental lubrication mechanisms from implant simulator studies as these have generally been developed to provide an assessment of the wear performance under realistic joint kinematics and loading. The range of loads and speeds experienced by the articulating contact region mean it highly likely that the lubricant film formation mechanism will also vary. The other variant is test time; there is ample evidence of structural and compositional changes to the articulating surface and subsurface, particularly during the 'running-in' period (Wang, 1998; Wimmer, 2003; Pourzal, 2009a; 2009b). Thus it is likely the wear mechanisms will also change again complicating the interpretation of results.

We have proposed a new lubricating mechanism for model synovial fluid which is based on the formation of a high viscosity protein-rich phase in the inlet to the sliding contact. This material forms, under some conditions, a much thicker film than predicted by the simple fluid models. Film formation is highly dependent upon the type of transient motion the bearing is subjected to, as this can either help or hinder the formation of inlet aggregates. The proposed lubrication mechanism has significant implications for the tribological performance and failure of artificial hips.

In recent years the design of "hard-hard" (CoM, MoM, CoC) hips has been driven by classical lubrication models derived from our understanding of mineral oil-based tribology (Dowson and Jin, 2006b; Jalali-Vahid *et al*., 2006; Jin, 2006). The move from MoP to MoM and CoC derives from the principle embodied in the Archard-wear law (Archard, 1953; Unsworth, 2006) that hard materials wear less. The increased head diameter and lower diametral clearance result in higher sliding speeds and lower contact pressures. As a result EHL equations predict increased film thickness, therefore increasing the "fluid film" thickness and hence the lambda value to >3 for most of the gait cycle.

The effect of different design and patient factors on film thickness for different lubrication mechanisms is summarised in Table 2. For all mechanisms a reduction in contact pressure is beneficial and this might explain the improved wear results obtained for LHMoM in simulator tests (Tipper *et al*., 2005). One of our observations is that the PAL film thickness decreases significantly with increasing contact pressures (Myant et al., 2012). However, the effect of increased sliding speeds is not so easy to predict. Our results (Myant *et al*., 2012) indicate that film thickness change with speed depends on the protein concentration and hence will be affected by patient SF composition. For high protein concentrations commonly associated with OA or periprosthetic SF the PAL film tends to decrease with speed. Clearly once the dominant mechanism moves away from simple EHL fluids the effect of synovial fluid composition becomes important and this will vary significantly from patient to patient. At present this variation is not captured in the screening process with BCS fluid.

7 Conclusions

The paper has examined lubricant film formation mechanisms in MoM hip joints. The following conclusions are drawn:

1. Artificial implants currently represent one the most difficult problems in tribology: transient loads and speeds coupled with a complex, multicomponent lubricating fluid.
2. The assumption that implant lubrication can be described by classical film formation mechanisms is too simplistic. These models were developed for single phase hydrocarbon fluids with Newtonian rheology.
3. The use of classical EHL models to predict SF film thickness in artificial hips is flawed and is not a good basis for implant design.
4. Protein-containing fluids (SF, BCS) aggregate in shear flow to high viscosity phases which are entrained into the contact zone to form separating films. We consider this to be an important film formation mechanism which we have termed PAL.
5. PAL shear-aggregation is the origin of the precipitates found in simulator tests and the deposits formed on implant surfaces.

ACKOWLEDGEMENTS

The authors wish to thank the UK EPSRC for funding this research: "In Contact Analysis of Synovial Fluid Lubricating Film Properties" (EP/H020837/1) and Platform Grant "Nanotribology: Measurement and Modelling across the Rubbing Interface" (EP/G026114/1).

REFERENCES

Archard, J.F., 1953. Contact and rubbing of flat surfaces. J. Appl. Phys. 24, 981-988.

Bergmann, G., et al., 2010. Realistic loads for testing hip implants. Bio-medical materials and engineering. 20, 65-75.

Bowsher, J.G., *et al.*, 1999. Metal-on-metal hip simulator study of increased wear particle surface area due to 'serve' patient activity. Proc Instn Mech Engrs Part J. 220, 279-286.

Bowsher, J.G., *et al.*, 2009. What Is a ''Normal'' Wear Pattern for Metal-on-Metal Hip Bearings? Journal of Biomedical Materials Research Part B: Applied Biomaterials. 297-308.

Brown, S.S, Clarke, I.C., 2006. A review of lubrication conditions for wear simulation in artificial hip replacements. Tribology Transactions, 49, 72-78.

Burgett, M., et al., 2013. FTIR Reflection-Absorption Spectroscopy Analysis of Organic Films on Explanted Metal Hip Joints. Submitted to Tribology International 2013.

Cooke, A.F., et al., 1978. The rheology of synovial fluid and some potential synthetic lubricants for degenerate synovial joints. Engineering in Medicine. 7, 66-72.

Delecrin, J., *et al*., 1994. Changes in joint fluid after total arthoplasty. Clin. Orthop. Rel. Res. 307, 240-249

Dowson, D., *et al*., 2004. A hip joint simulator study of the performance of metal-on-metal joints. Part II: design. J. Arthroplasty, 19, 124–130.

Dowson, D. 2006a. Tribological principles in metal-on-metal hip joint design. Proc. IMechE Part H. 220, 161-171.

Dowson, D., Jin, Z., 2006b. Metal-on-metal hip joint tribology. Proc Instn Mech Engrs Part H. 220, 107-118.

Dwyer-Joyce, R.S. 1999. Predicting the abrasive wear of ball bearings by lubricant debris. Wear. 233-235, 692-701.

Essner, A., Sutton, K., Wang, A. 2005. Hip simulator wear comparison of metal-on-metal, ceramic-on-ceramic and crosslinked UHMWPE bearings. Wear. 259, 992-995.

Fan, J., *et al*., 2011. Inlet protein aggregation: a new mechanism for lubricating film formation with model synovial fluids. Proc Instn Mech Engrs Part H. 25, 696-709.

Fisher, J., *et al*., 2004. Wear of surface engineered metal-on-metal hip prostheses. J. Mater. Sci.: Mater. Med. 15, 225-235.

Gale, L.R., *et al*., 2007. Boundary lubrication of joints Characterization of surface-active phospholipids found on retrieved implants. Acta Orthopaedica. 78, 309–314

Glovnea, R.P., Spikes, H.A., 2000. The Influence of Lubricant Upon EHD Film Behavior During Sudden Halting of Motion. Tribology Transactions, 43, 731 - 739

Glovnea, R.P., Spikes, H.A., 2002. Behavior of EHD Films During Reversal of Entrainment in Cyclically Accelerated/Decelerated Motion. Tribology Transactions, 45, 177 – 184

Hart, A.J., *et al*. 2006. The association between metal ions from hip resurfacing and reduced T-cell counts. Journal of bone and joint surgery. 88-B, 449-454

Hills, B., 2000. Boundary lubrication in vivo. Proc Instn Mech Engrs Part H. 214, 83-94

Hirst, W., Hollander, A.E., 1974. Surface finish and damage in sliding. Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences. 337, 379-394

Hooke, C.J., 1980. The elastohydrodynamic lubrication of heavily-loaded point contacts. Jour Mech Eng Sci. 22, 183-187.

Isaac, G.H., et al., 2006. Metal-on-metal bearings surfaces: materials, manufacture, design, optimization, and alternatives. Proc. IMechE Part H. 220,119-133.

ISO 14242-1, 2012. Implants for surgery - Wear of total hip-joint prostheses - Part 1: Loading and displacement parameters for wear-testing machines and corresponding environmental conditions for test.

Jalali-Vahid, D., et al., 2006. Effect of start-up conditions on elastohydrodynamics lubrication of metal-on-metal hip implants. Proc Instn Mech Engrs Part H. 220, 143-150

Jin, Z., 2006. Theoretical studies of elastohydrodynamic lubrication of artificial hip joints. Proc Instn Mech Engrs Part H. 220,719-727

Kaddick, C., Wimmer, M.A., 2001. Hip simulator wear testing according to the newly introduced standard ISO 14242. Proc Instn Mech Engrs Part H. 215, 429-442.

Katti, K.S. 2004. Biomaterials in total joint replacement. Colloids and Surfaces B: Biointerfaces. 39, 133–142

Kitano, T., et al., 2001. Constituents and pH changes in protein rich hyaluronan solution affect the biotribological properties of artificial articular joints. J. Biomechanics. 31, 1031-7.

Klein, J., 2006. Molecular mechanisms of synovial joint lubrication. Proc Instn Mech Engrs Part J. 220, 691-710.

Liao, Y.S., *et al.*, 1999. Effect of protein lubrication on the wear properties of materials for prosthetic joints. J Biomed Mater Res. 48, 465-473.

Lubrecht, T., et al., 2001. Starved elastohydrodynamic lubrication theory: Application to emulsions and greases. Comptes Rendus de l'Academie des Sciences - Series IV: Physics, Astrophysics. 2, 717-728.

Maskiewicz, V.K., et al., 2010. Characterization of protein degradation in serum-based lubricants during simulation wear testing of metal-on-metal hip prostheses. J. of Biomedical Mat. Res - Part B Applied Biomaterials. 94, 429-440.

Mavraki, A., Cann. P., 2011. Lubricating film thickness measurements with bovine serum. Trib. Int. 44, 550-6.

Medley, J.B., et al., 1997. Kinematics of the MATCO@ hip simulator and issues related to wear testing of metal–metal implants. Proc Instn Mech Engrs Part H. 211, 89-99.

MHRA. 2010. Medical Device Alert, April.

Myant, C., et al., 2012. Lubrication of metal-on-metal hip joints: The effect of protein content and load on film formation and wear. Journal of the mechanical behaviour of biomedical materials. 6, 30-40.

Myant, C., Cann, P. 2013. In contact observation of model synovial fluid lubricating mechanisms. Tribology International. 63, 97-104

National Joint Registry, 2012. 9th Annual Report.

Oates, K., *et al*., 2006. Rheopexy of synovial fluid and protein aggregation. Journal of the Royal Society Interface. 3, 167-174.

Pourzal, R., et al. 2009a. Micro-structural alterations within different areas of articulating surfaces of a metal-on-metal hip resurfacing system. Wear. 267, 689-694.

Pourzal, R., et al. 2009b. Subsurface changes of a MoM hip implant below different contact zones. J. Mechanical Behaviour of Biomedical Materials. 2, 186-191.

Revell, P.A., et al., 1997. Biological reaction to debris in relation to joint prostheses. Proc Instn Mech Engrs Part H. 211(2), 187–197.

Rigney, D.A., 2000. Transfer, mixing and associated chemical and mechanical processes during the sliding of ductile materials. Wear. 245, 1-9.

Roba, M., *et al.,* 2009. The adsorption and lubrication behavior of synovial fluid proteins and glycoproteins on the bearing-surface materials of hip replacements. Biomaterials. 30, 2072–2078

Schwarz, I., and Hills, B., 1998. Surface-active phospholipid as the lubricating component of lubricin. Rheumatology. 37, 21-6.

Shetty, V.D., Villar, R.N., 2006. Development and problems of metal-onmetal hip arthroplasty. Proc Instn Mech Engrs Part J. 220, 371-377.

Stachowiak, G.W., Batchelor, A.W., 2005. Engineering Tribology. Elsevier.

Spikes, H.A., 1999. Thin films in elastohydrodynamic lubrication; the contribution of experiment. Proc Instn Mech Engrs Part J. 213, 335-352.

Sugimura, J., Spikes, H.A., 1996. Technique for measuring EHD film thickness in non-steady state contact conditions. Elastohydrodynamics. Proceedings of the 23rd Leeds–Lyon Symposium on Tribology (Eds D. Dowson et al.).

Swann, D.A., and Radin, E.L., 1972. The Molecular basis of articular lubrication. I. Purification and properties of a lubricating fraction from bovine synovial fluid. J Biol Chem. 247, 8069-73.

Swann, D.A., et al., 1974. Role of hyaluronic acid in joint lubrication. Ann. Rheum. Dis. 33, 318-26.

Tadmor, R., Chen, N., and Israelachvilli, J., 2003. Normal and Shear Forces between Mica and Model membrane Surfaces with Adsorbed Hyaluronan. Macromolecules 36, 9519-9526.

Tipper, J.L., *et al.,* 1999. Quantitative analysis of the wear and wear debris from low and high carbon content cobalt chrome alloys used in metal on metal total hip replacements. J. Mater. Sci.: Mater. Med. 10, 353–362.

Tipper, J., *et al.,* 2005. The science of metal-on-metal articulation. Current Orthopaedics. 19, 280-287

Underwood, R.J., et al., 2012. Edge loading in metal-on-metal hips: Low clearance is a new risk factor. Proc Instn Mech Engrs Part H. 226, 217-226

Unsworth, A., 2006. Tribology of artificial hip joints. Proc Instn Mech Engrs Part J. 220, 711-718.

Varano, R., Bobyn, J.D., Medley, J.B., Yue, S. 2006. The effect of microstructure on the wear of cobalt-based alloys used in metal-on-metal hip implants. Proc. IMechE Part H: J. Eng. in Medicine. 220, 145-159

Wang, A., *et al.,* 1998. Lubrication and wear of ultra-high molecular weight polyethylene in total joint replacements. Trib. Int. 31, 17-33.

Wang, A., *et al.,* 2004. The effects of lubricant composition on in vitro wear testing of polymeric acetabular components. J. Biomed. Mater. Res. 68B, 45–52.

Wimmer, M.A., et al., 2003. Tribochemical reaction on metal-on-metal hip joint bearings. A comparison between in-vitro and in-vivo results. Wear. 255, 1007–1014

Wroblewski, B.M., Siney, P.D. 1993. Charnley low- friction arthroplasty of the hip—long term results" Clin. Orthop. Related Res. 292, 191–201

Yao, J.Q., et al., 2003. The influences of lubricant and material on polymer/CoCr sliding friction. Wear. 255, 780–784

Lubricant type	Total Protein (g/l)	Albumin (g/l)	Globulin (g/l)	pH
Healthy SF	18-20	7-18	5-29	7.3-7.43
Periprosthetic SF	30-50	20-39	5-15	7.5-8.5
Osteoarthritis	30-32	18-19	13-13.5	7.4-8.1
Rheumatoid arthritis	35-45	16-26	15-25	6.6-7.6
Bovine Calf Serum	58-72	4	6	7-8.1

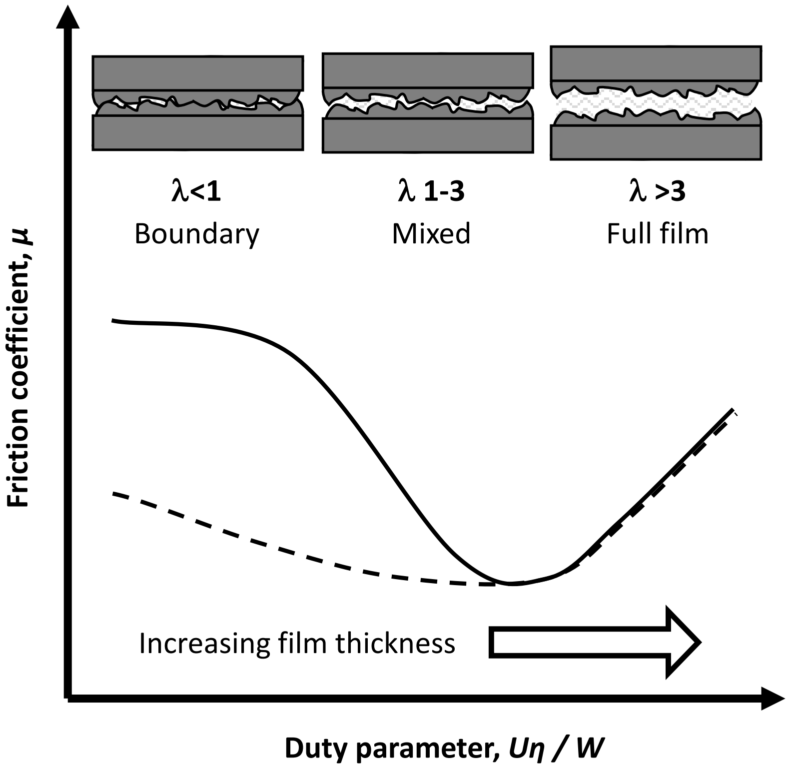
Table 1 Synovial fluid composition (Kitano et al., 2001; Wang et al., 2004)

Implant Factors	EHL	Boundary	PAL
Design			
Reduced pressure	Positive	Positive	Positive
Increased sliding speed	Positive	Negative	Negative [1]
Materials			
Mechanical	Important	Less important	Less important
Surface chemistry	Less important	Important	Important[2]
Synovial fluid properties			
Chemistry	Less important	Important	Important
Bulk Viscosity	Important	Less important	Less important

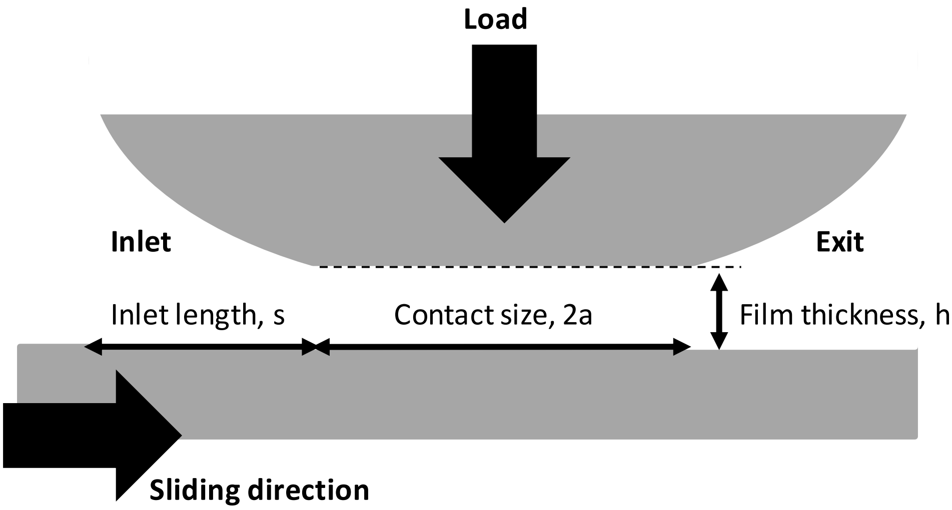
[1] Depends on protein concentration, [2] Adherence

Table 2 Implication of MoM design and patient factors on film formation with different lubrication mechanisms

Figures

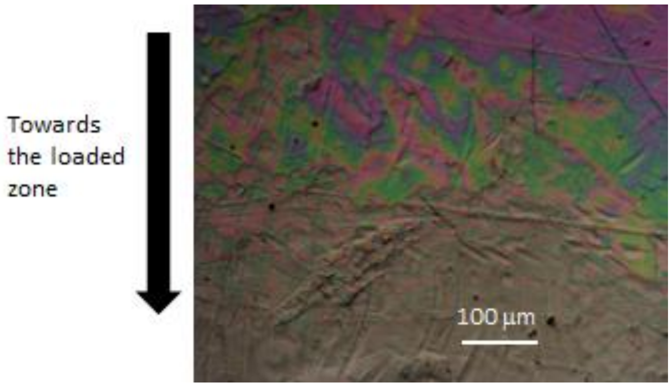


(a) Simple representation of a Stribeck curve for an oil (solid line = no boundary additive, dashed line = boundary additive) and different lubrication regimes

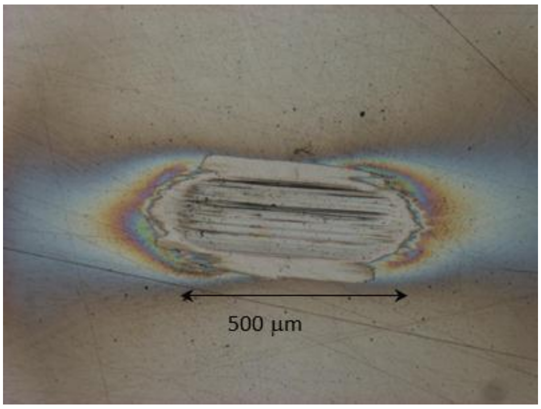


(b) Representation of a sliding contact

Figure 1. Lubrication fundamentals: Stribeck curve and regions of a lubricated contact



(a) Explanted femoral head – scratches and deposited protein films at the edge of wear zone [for further example see Burgett 2013]



(b) Wear scar and protein deposit from reciprocating ball-on-flat test. Deposited protein films are seen at either end of the stroke.

Figure 2. Images from (a) explanted metal femoral head (b) wear scar and protein deposits from laboratory test.

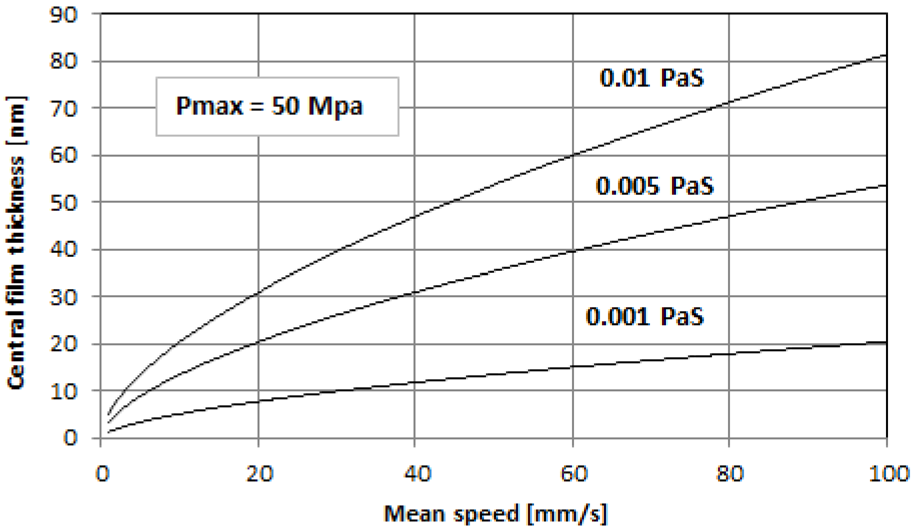


Figure 3. Calculated film thickness (Eq. 2) plotted against mean speed for different viscosity simple fluids.

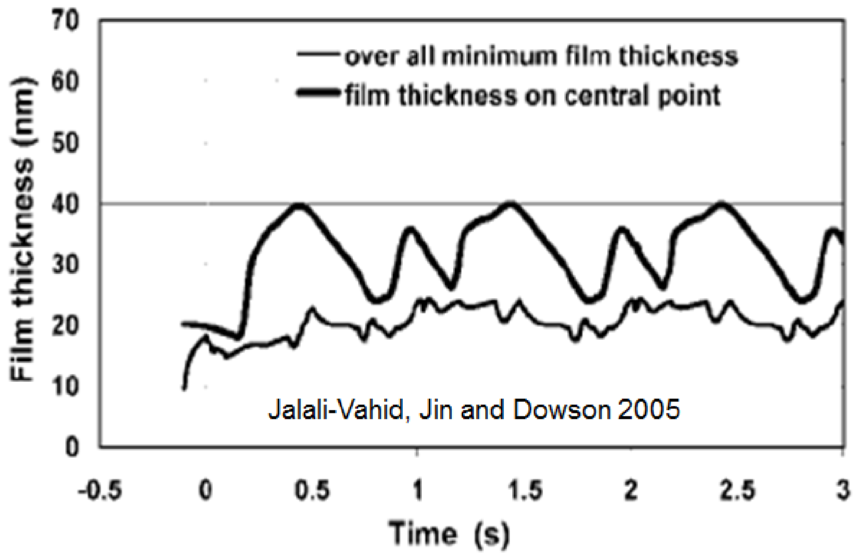


Figure 4. Predicted film thickness values over several gait cycles (Jalali-Vahid *et al*., 2006).

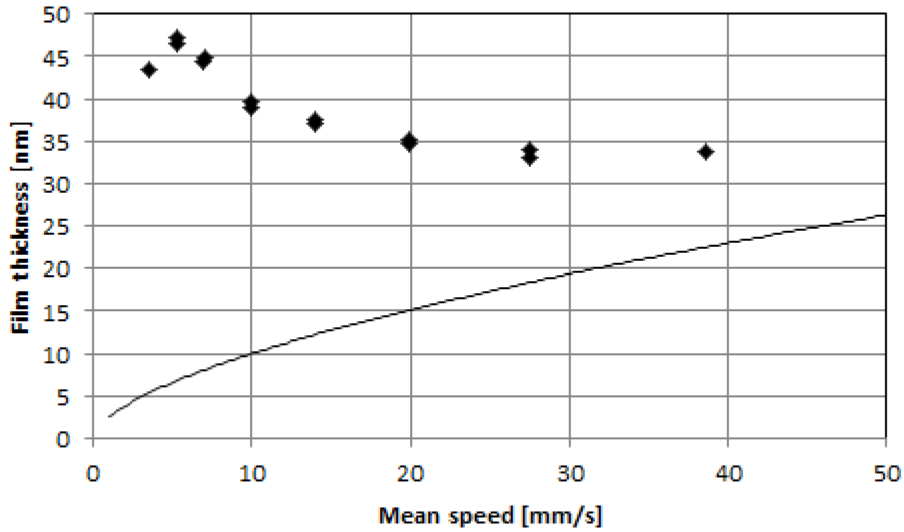


Figure 5. Optical interferometric film thickness measurements against speed for 25% w/w BCS solution (black markers) theoretical predictions (black line) from Eq. 2 are also plotted for a simple Newtonian fluid (η = 0.01 Pas).

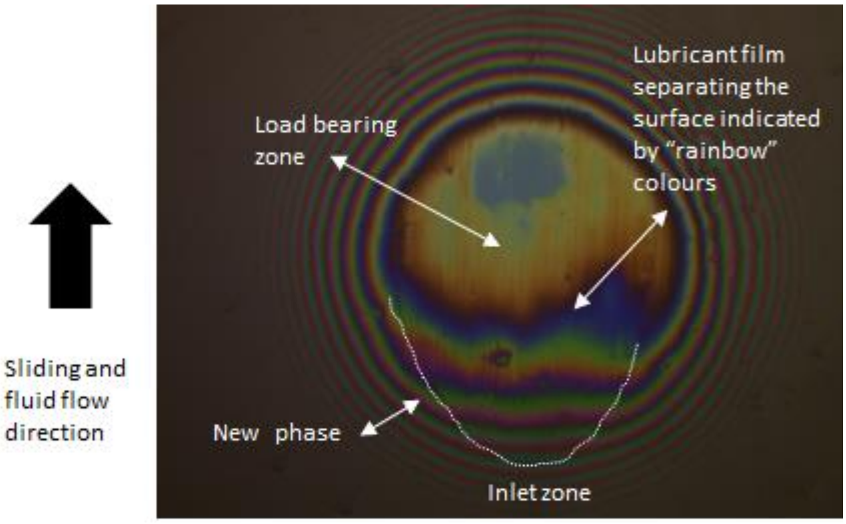


Figure 6. Formation of a new phase in the inlet zone of a sliding contact

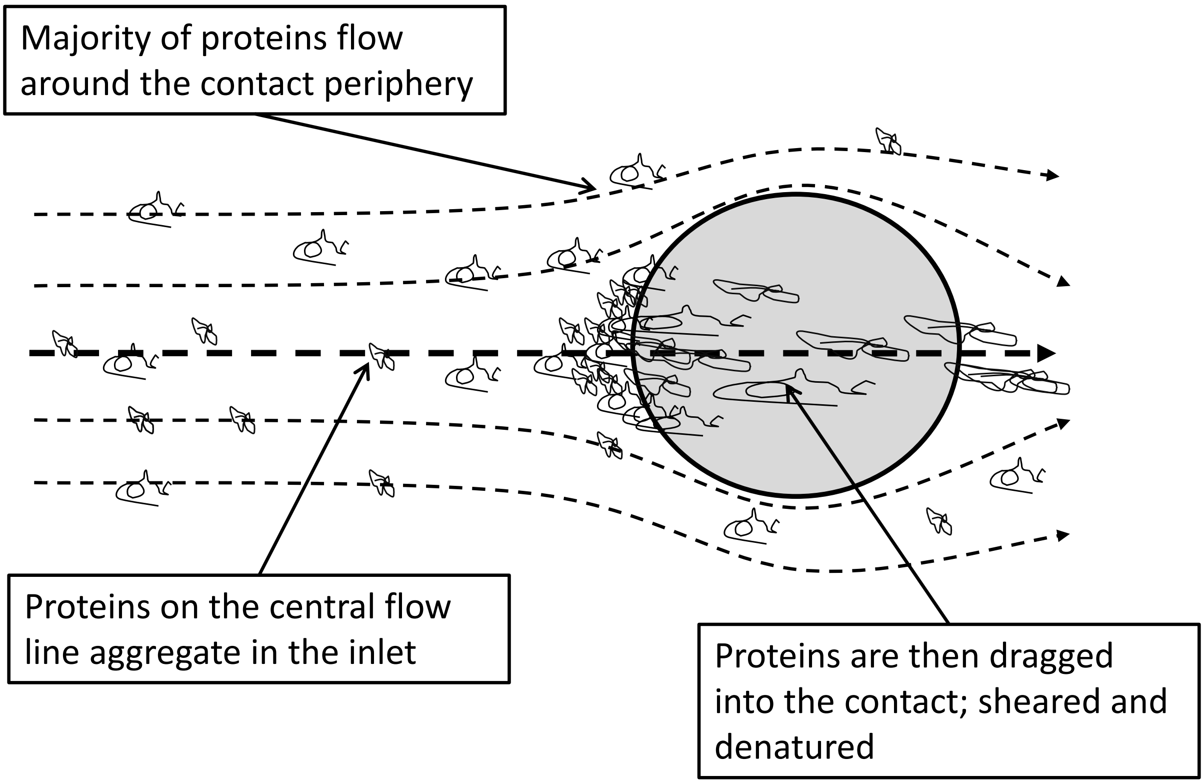


Figure 7. Sketch of contact flow lines

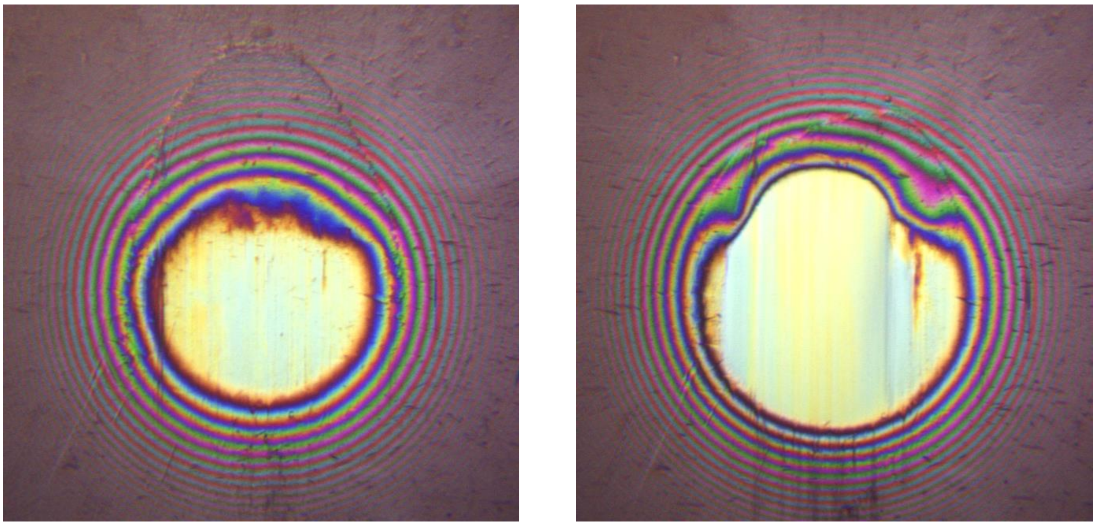


Figure 8. Optical interference images of the contact zone at U = 10 (LHS) and 50 (RHS) mm/s. The inlet is at the top of the contact zone. The protein rich inlet region is visible above the main contact region by the discontinuity in the interference fringes.

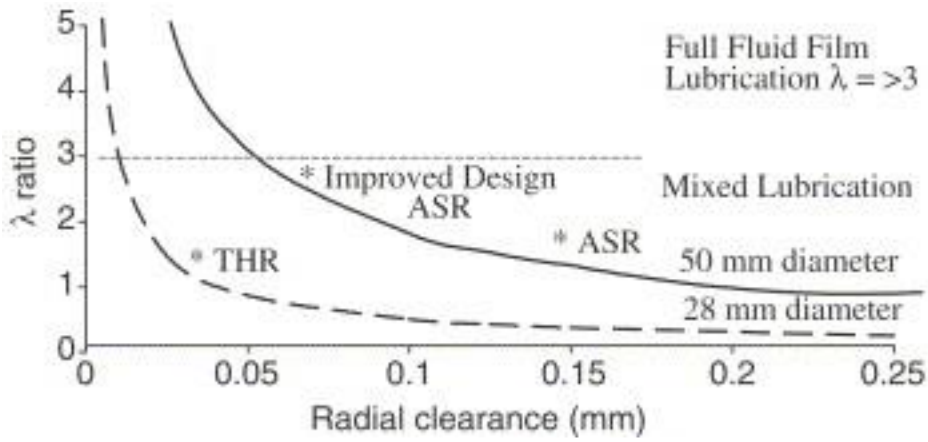


Figure 9. The effect of radial clearance (half of diametral clearance) upon lubrication and λ ratio in metal-on-metal total hip implants and resurfacing prostheses (ASR, DePuy Int.). (Tipper *et al.,* 2005).