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# 4. Unification of friction and wear

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**Abstract.** Friction and wear are often treated as unrelated, distinct phenomena. In fact, friction and wear are macroscopic manifestations of common physical processes operative at sliding interfaces. Friction and wear are related through the physics of these processes, which are thermodynamically irreversible and dissipative, since energy loss is almost always involved. This chapter attempts to unify friction and wear, by focusing on the dissipative processes found at sliding interfaces. Prominent mechanisms of friction and wear are first reviewed, with goal of identifying the associated dissipative processes. The laws of thermodynamics are then reviewed, with a focus on entropy generation and the first and second laws. This is followed by review of the Degradation-Entropy Generation theorem, which relates degradation of any form to the irreversible entropy generated by responsible dissipative processes. The theorem is applied to sliding interfaces and a tribological control volume, to relate wear to responsible interfacial dissipative processes. Friction force is also related to entropy generated by interfacial dissipative processes. Next, dissipative processes associated with friction and wear, and found at sliding interfaces, are identified and reviewed, and the entropy generated by these dissipative processes is presented. Finally, conclusions regarding friction and wear, relations to dissipative processes, are presented.

## 1. Introduction

Friction and wear have classically been treated as unrelated, distinct phenomena [1, 2, 3]. This view persists. Even Tribology often classifies friction and wear separately. In 1965, Rabinowicz [3] suggested why: "Friction is usually classified as a branch of Physics, or of Mechanical Engineering. Wear is often considered to be part of Metallurgy." In reality, friction and wear are manifestations of the same interfacial physics and events, and consequently, friction and wear often depend on the same phenomenological variables. A vivid example of this interdependency is Hwang *et al.*'s [4] measurements of friction coefficient with simultaneous photography of wear particle formation and detachment. Both friction and wear are

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associated with, or induced by, dissipative irreversible processes that dissipate mechanical power, reorder the material structures of the bodies, and generate entropy. Indeed, friction force usually provides the energy that induces wear.

This was recognized by Czichos [5] who advocated a systems approach to tribology. Systems approaches [6, 7] typically emphasize balance or conservation of energy, power flows, mass, and other fundamental quantities of physical systems. Czichos [5] cited various "planes"—functional, work, thermal, and material—for these balance and conservation applications to tribology. Of particular interest to this article, Czichos identified dissipative processes of friction and wear, and states on page 42, "The processes on and between the material planes are likely to involve entropy changes, generally the production of entropy...".

This chapter will review friction and wear, with focus on showing dependencies and relationships. Past reviews [8, 9, 10, 11] of friction and wear have generally focused on physical mechanisms of friction and wear. The theme of this review is to unify friction and wear, by identifying and highlighting the dissipative irreversible processes germane to both. This chapter will review friction, wear, the thermodynamic underpinnings between friction force and degradation by wear, and the more important associated dissipative processes common to both. The goal is to show that by identifying, studying, and understanding these underlying irreversible processes, friction and wear can be related, and predicted.

## 2. Friction

Friction force [12] is a non-conservative and dissipative reaction force between two bodies in relative motion, tangential to the interface between the bodies, with force direction always opposing motion. Suh [13] stated "the external work done by the friction force must be equal to the sum of the internal energy increase and the energy dissipated at and near the interface." Friction, a principal cause of power loss, converts usable work into heat and produces entropy. Friction is dissipative in the thermodynamic sense [14]. Dissipative processes, driven by energy of friction force, induce irreversible changes in surface morphology and composition. Dissipative processes associated with friction and wear include hysteresis associated with asymmetries of adhesion [15], movement of dislocations and plastic deformation from surface plowing, surface and subsurface fracture of surfaces [13], strain hardening of metallic surfaces during sliding, phase changes induced by friction heating or mechanical stresses, and mixing or transfer of material. Friction force can arise from many complex and diverse effects, including surface adhesion followed by surface rupture or tearing, surface and near surface deformation, surface gouging, surface plowing, asperity interaction, film

cracking and rupture, and lubricant shear, among others. Friction can depend on numerous phenomenological variables. Dominant factors [13] include kinematics of the surfaces in contact; applied external loads and/or displacements; environmental conditions such as temperature, pressure, humidity, chemistry, and presence of lubricants; surface topography and roughness, surface geometry, and environment; materials of slider (first body) and counter-surface (second body); material properties of these bodies; deformations of slider and counter-surface; and presence of surface films, lubricants (solid, liquid and gas), and third bodies [16] (such as entrapped wear debris or accumulated material from surface films, or transferred material from one body to another).

In reference to the Stribeck curve for lubrication [17], friction has been classified as dry, where surfaces slide without intervening lubricants, allowing direct contact between asperities; boundary lubricated, where surfaces contact but thin films adhered to one or both surfaces protect underlying material; mixed film, where lubricant films partially separate surfaces, and reduce surface contact; and hydrodynamic wet film, where pressures developed from viscous shearing of fully developed lubricant films separate surfaces, and prevent surface contact. Friction force is largest for dry friction, and reduces with boundary lubrication, mixed film lubrication, and hydrodynamic lubrication in that order. The focus of this chapter is dry and boundary lubricated friction.

Classical models dating to DaVinci and Coulomb found friction independent of apparent area of contact and proportional to normal force. The Coulomb-Amontons friction law

$$F = \mu N \tag{1}$$

relates friction force $F$ to normal force $N$, via the coefficient of friction $\mu$. Friction force often depends at least weakly on sliding speed $v$, the difference between surface velocities. Observations of dry sliding identify a static friction force $F_s$ and coefficient $\mu_s$, applicable for $v = 0$, and a kinetic friction force $F_k$ and coefficient $\mu_k$, valid for large $v$. Since usually $F_s \geq F_k$, continuity suggests $F = F(v)$ to be monotonically decreasing. Ovcharenko *et al.* [18] observed static friction force at the inception of sliding for lightly to heavily loaded steel and copper spheres sliding on sapphire. Static friction coefficient depended on real contact area, normal force, and deformation mode. Kinetic friction, which is dissipative and involves power loss, induces heating, higher temperatures, material changes, stress, cracking, fatigue, and morphological changes of surfaces. Attempts to classify kinetic friction force [10, 9, 13] identified mechanisms of adhesion, plowing, surface fatigue, tribochemical actions, delamination [13], and effects of surface films [10]. Suh [13] estimated friction force for sliding of metals via mechanics of

asperity adhesion, shearing and plowing. These mechanisms assumed irreversible plastic deformations coupled friction force and energy dissipation. For any system, multiple mechanisms of friction force are simultaneously present. Which type of friction dominates depends on conditions. The total friction force, friction coefficient [13, 9], and work of friction

$$F = \sum_j F_j, \quad \mu = \frac{F}{N} = \sum_j \mu_j \,, \quad W^{\mu} = \sum_j W_j^{\mu} \tag{2}$$

are the sum over all friction components. Conditions can cause one or more components of friction in the sums to dominate. For low speed dry sliding of metals, friction force is often dominated by adhesion and plowing components. The remainder of this section will introduce types of friction force and associated dissipative processes.

## 2.1. Adhesion component of friction

Bodies pressed into contact by forces oriented along the normal to the interface tend to adhere upon separation. Indeed, after removing a compressive force, a tensile force normal to the surface is often needed for full separation. Adhesion can be due to "cold welding" from a variety of bonding types, such as chemisorption caused by strong atomic bonding (metallic, ionic or covalent), physisorption due to intermolecular forces such as van der Waals forces [19, 20], or hydrogen bonding. Adhesion influences normal and tangential contact forces between bodies [21, 20, 22, 23], especially at length scales of order of nanometers to microns. Surface films affect adhesion. Adhesion can be strengthened or inhibited, depending on the type and nature of the film. Very strong adhesion requires bare surfaces. Wipe of surface films or tearing off of material on surfaces exposes underlying atoms to stronger metallic, ionic or covalent bonding with atoms on the opposing surface.

Bodies pressed into contact develop a real area of contact considerably smaller (tens to hundreds of times smaller) than the apparent area of contact [24, 25]. The deformations that develop the real area of contact can be elastic for lightly loaded contacts with plasticity index $\psi = (E'/H)\sqrt{\sigma_s/R'} \leq 0.6$, but for contacts with $\psi \geq 1$ or $0.6 < \psi < 1$ with heavy load, asperity deformations are principally plastic [24, 25], and the real area of contact $A_r \approx N/H$. Here $N$ is the contact force normal to the contact surface, $\sigma_s$ is the standard deviation of the surface heights, usually assumed to have Gaussian distribution, $1/E' = (1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2$ is the equivalent elastic modulus and $1/R' = 1/R_1 + 1/R_2$ is the equivalent curvature between contacting asperities of bodies 1

and 2, and $H$ is the Meyer hardness [26, 27]. After removing the contact loads, attractive forces at the interface tend to maintain contact [25]. Indeed, tensile forces, albeit small, are often required to fully separate the surfaces. These surfaces attractions, due to intermolecular forces [19, 20] are most pronounced on length scales of order of hundreds of nanometers or less. The overall effects of these multiple attractive forces can be lumped into surface energy $\gamma$, the work per unit area needed to create the surface, defined in section 5.4.1. During contact, the adhesive forces tend to augment the real area of contact. Johnson [21] reviewed adhesion, and how it enlarges contact area. The presence of a condensed liquid film increases the pull-off force needed to separate bodies [21, 20, 23].

Adhesive effects increase friction force, discourage separation of contact areas, and change dynamic response [22]. Bowden and Tabor's [8] early model of adhesion friction envisioned asperities on opposing surfaces contacting, cold welding (or adhering), and rupturing due to tangential forces imposed during sliding. The tangential force $F = SA_r \approx SN/H$, where the junction adhesive shear strength $S$ depends on the thermodynamic work of adhesion, see section 5.4.1. The coefficient of friction for adhesion $\mu_a = F/N = S/H \approx 0.2$ [8, 13], since hardness $H$ for metals is five to six fold the shear strength $S$. Surface films, which interfere with asperity to asperity contact, tend to reduce adhesion and adhesion friction. Suh [13] improved Bowden and Tabor's estimate using better models of asperity plasticity. Straffelini [28] extended the adhesive junction strength theory, to include plastic deformation, chemical reactions and other irreversible phenomena occurring at the asperities during adhesion and shear.

## 2.2. Plowing coefficient of friction

Asperities of a harder surface, or hard abrasive particles trapped between surfaces (associated with abrasive wear), can plow a softer counter-surface during sliding. The front of a "plow" digs a groove or furrow and displaces material to the sides of the wear track. For ductile metals, the principal dissipative process is plastic deformation. Suh [13] viewed an asperity as a rigid cone with aperture angle $\phi = \pi/2 - \theta$ plowing a v-shaped groove of width $w$ and angle $2\phi$ through a rigid perfectly plastic counter body. With tangential and normal forces $F = Pw^2[\tan\theta + (s/P)\sec\theta]/4$ and $N = P\pi w^2/8$ equilibrating pressure $P$ and shear stress $s$ on the front of the cone, the plowing coefficient of friction $\mu_p = F/N = 2/\pi(\tan\theta + s/P \sec\theta)$. The first term was derived by Bowden and Tabor [8]. With $10^\circ \le \theta \le 40^\circ$ estimating the range of typical asperity slopes, pressure $P$ estimated by hardness $H$ which is five to six times shear strength $S$, then for $s/S$ between zero and one, $0.1 \le \mu_p \le 0.6$.

Komvopoulos *et al.* [29, 30, 31, 32] studied friction and wear of like metals sliding under boundary lubrication and dry [33] conditions. For aluminum, copper, and chromium specimens, pin on disk tests produced grooves typical of plowing. Since the specimens were initially smooth and clean, the authors hypothesized that wear particles shed from the surfaces formed, became entrapped within the sliding interface, strain hardened, and functioned as plows. Analytical estimates of friction coefficient [33] and wear volume, derived from plasticity based models of microscopic "plows" cutting out material, compared well with their measurements of friction and wear. Inspection of surfaces also suggested little adhesion. Surface films tend to avoid adhesive junction welding, moderate stress fields beneath sliders, and avoid surface damage due to plastic damage from plowing [31, 32]. These films can be self-forming, such as surface oxides [31], or applied hard TiN coatings [32]. Removal or disruption of these films permitted plowing [31, 32] with concomitant high friction and wear.

### 2.3. Other components of friction force

Various other components of friction exist, related to dissipative interfacial processes with dependence on distance slid $x$. For example, an asperity ratchet mechanism of friction force [34, 15] has interacting roughness on opposing surfaces with asperity geometries that permit asperities on one surface to climb up and fall down asperities on the other surface via different process paths, forming a hysteresis. The third body, see section 5.1 is a principal site of dissipation. Material entrapped between sliding first bodies is heavily worked by the mechanical energy dissipated by friction force.

## 3. Wear

Wear is loss of material from surfaces of bodies [2, 3]. Most wear requires rubbing, but wear can also be induced by non-rubbing processes such as erosion or thermally induced fracture. Sliding wear is caused by rubbing between bodies in relative motion. Wear is usually defined as the volume of material removed from a surface, but other forms of surface damage can be classified as wear, such as movement of material over a surface (due to plastic deformation or detachment), transfer of material from one surface to another, and cracking of surfaces. In all cases, wear is an irreversible process that involves permanent movement of atoms and long term degradation of the surface and underlying body. Wear can depend on numerous phenomenological variables, including geometry and kinematics of bodies, relative motion such as vibration [35, 36, 37] between bodies, force or load, sliding speed, distance slid, power dissipated, material combinations,

environment (temperature, humidity, vibrations, chemistry, atmosphere, contaminants, surface deposits, etc.), and presence of third body materials, among others. Wear removes material from surfaces, which compromises tolerances and fits of machine components. Wear debris can migrate and contaminate other parts of a machine.

Wear is commonly measured in terms of mass loss (via weight loss), volume loss, or surface recession (reduction in length of a specimen of constant cross section). When mass loss is too difficult or inconvenient to measure, wear can be estimated as amount of surface damage such as size of wear scar geometry, or estimated by the amount the wear debris shed from a surface. Wear measurements can exhibit large variability. Results from different locations and/or times can vary as much as 50 to 1000 percent. Causes of variability include slight differences in environmental conditions (e.g., temperature and humidity), kinematics of the test machine [3], and vibrations [35, 38, 36, 37], among others. Since most sliding wear is mild to moderate, tests can require several hours to days to accumulate enough wear for a reliable measurement. Consequently, wear measurement are usually expensive relative to other material measurements.

Sliding wear occurs by many different physical mechanisms [8, 2, 9, 13, 10, 39]. Tabor [10] sorted wear of metals and ceramics into mechanisms of adhesion, grooving and cutting, fracture or cracking (more important for brittle ceramics), friction heating, and chemical effects, and wear of polymers into mechanisms of adhesion, grooving and cutting, and heat induced surface softening and melting. Recently, Kato [39] grouped wear into mechanical, chemical and thermally induced forms, and identified abrasive, adhesive, flow, fatigue, corrosive, melt, and diffusive wear modes, with dominant wear processes of fracture, plastic flow, liquid flow, dissolution, oxidation, and evaporation. Kato identified ”physical adsorption, chemical adsorption, tribochemical activation, tribofilm formation, oxidation and delamination, oxidation and dissolution, oxidation and gas formation, phase transition, recrystallization, crack nucleation and propagation, and adhesive transfer and retransfer” (of material to and from bodies) as principal physics and chemistry of wear. Suh [13] classified wear into adhesive, abrasive, surface fatigue, tribochemical, and delamination modes. Each of these forms of wear involves a different physio-chemical mechanism with a different set of dissipative processes operative at the interface. Ludema [40, 41] noted that wear models formulated before 1995 involved many diverse wear mechanisms, many different physical principles, and many variables.

Similar to equation (2), the total wear $w$ can be viewed [39, 13] as a sum

$$w = \sum_j w_j \tag{3}$$

of components from multiple wear mechanisms $w_j$ present and operative at a sliding interface. Conditions (e.g., speed, load, environment) can favor one mechanism of wear to dominate the sum, and marked changes in wear rate can be observed. The conditions that trigger transitions in wear rates are of particular interest to machine designers. Wear maps identify operating and environmental conditions for severe, moderate, and low wear. Wear maps plot curves of constant wear rate in a multi-axis space, where the axes indicate the intensity of physical variables such as speed, temperature, load, and humidity. Wear maps associate levels and/or modes of wear with physical conditions. Boundaries between regions graphically identify the conditions for transitions in wear. Hsu and Shen [42] developed wear maps for ceramics. Maeda *et al.* [43] developed wear maps for rubber, and showed that scratch wear of rubber depended on adhesion, deformation, and energy dissipated by friction. Deformation depended on viscoelastic properties, tearing depended on static strength properties. Briscoe et al [44, 45] reviewed a body of work involving lubricated polymer nano-coatings. Different materials, films, and lubricants were compared, and assessed. Measurements of wear and friction involved use of scratch tests. Deformation mechanisms were analyzed.

The remainder of this section will overview prominent mechanisms of wear, and identify the principal dissipative processes involved.

## 3.1. Adhesive wear

Adhesive wear is usually present, generally mild, and usually dominant at low speed. Suh *et al.* [30] attributed sliding wear of like metals to plowing and abrasive wear, but their experiments with initially clean surfaces likely generated hard abrasive particles via adhesive wear. Surfaces adhere through attraction from van der Waals forces, and sometimes stronger metallic bonding if surfaces are bare. During sliding, asperities on opposite surfaces approach, interfere, and bond or weld [8] to each other. The adhesive bonding can be caused by many effects discussed in section 5.4.1. Further sliding breaks the bonds, and can detach a wear particle of size 10 to 100 microns from the surface. To model sliding wear, Holm [26] and Archard [46, 47], each working independently, expressed the volume of material lost to wear

$$W = \frac{K}{H} NL \tag{4}$$

to the normal force $N$ pressing the bodies together, the distance slid $L$, the diamond pyramid hardness number (DPN) $H$, and a dimensionless wear coefficient $K$ that depends on material selection and environment [47]. Hardness $H$ balances the

dimensions of wear volume $w$ with phenomenological variables $N$ and $L$. Typical values of wear coefficient $K$ range from $10^{-5}$ to $10^{-3}$ for metals [3, 48]. Although Holm and Archard derived equation (4) by considering the probabilistic interaction of atoms, asperities, or contact regions between the sliding opposing surfaces, note that the product $NL$ has dimensions of energy. If equation (1) is substituted into equation (4),

$$w = \frac{K}{\mu H} FL = K'FL = K'W \tag{5}$$

where $K' = K/(\mu H)$. Equation (5) emphasizes the relation between wear and friction force. Implicit in equation (5) is an energy statement involving work $W = FL$ of friction force. Equation (4) was formulated for adhesive wear, but describes other mechanisms such as abrasive wear. Equation (4) can be revised to be consistent with other measurements of wear. For surface recession (loss of length from worn slider), divide $w$ by the cross section area $A$ of the slider.

During adhesive wear, asperity junctions adhere. Forces induced by subsequent sliding dissipate energy by rupturing and/or plastic deforming the adhered regions. These actions can tear off strips of material which can transfer to the counter surface, reattach to the slider, join the third body [16], or exit the sliding interface to become wear particles [49]. Spalling, galling, scuffing and seizure [10, 50] are severe forms of adhesive wear with large loss of material. These modes often involve changes in thickness, material structure, and composition of surface layers. Suh *et al.* [51] found a basic change in surface material composition of aluminum and cast iron discs (run against pins of similar material) at the onset of scuffing. The surface composition changed after protective coatings deteriorated, exposing underlying disc material to adhesion, seizure, and severe wear.

## 3.2. Abrasive wear

Abrasive wear is moderate to severe. Abrasive particles originating from the environment or generated by wear processes [30] can become entrapped within a sliding interface. As the slider moves over the counter surface, some of these abrasive particles become plows, cutters, or rollers, which can gouge, scratch, or indent the surfaces [52]. The much larger wear particles dug from the surface results in grooves, and a wear coefficient $K$, see equation (4), typically tens to thousands of times higher than adhesive wear. Abrasive wear can be modeled by equation (4), or more accurately by the Preston-Rabinowicz [3] equation, which is similar to Archard's law, equation (4). Metallic wear debris entrapped within the

interface join the third body. As proposed by Godet [16, 53], third body accommodates the velocity discontinuity generated by the slip velocity of sliding between the bodies. As such, the particles are subjected to forces from rolling, shear, and compression. The wear debris particles can work-harden due to plastic deformations imposed on the particles, as part of the third body. These hardened particles can become abrasive particles, causing an abrupt change in wear rate. Since abrasion involves mechanisms of plowing and machining, plastic deformation and creation of new surface are the major dissipative processes.

## 3.3. Fretting wear

Fretting involves rubbing between bodies with small amplitude, low frequency oscillatory motions [54]. Fretting degrades components through surface wear and structural fatigue. Fretting wear of metals involves intense plastic deformations near the surface of the wearing body, sometimes accompanied with corrosion or oxidation of material. Rise of bulk temperatures are usually moderate, of order of tens of degrees Kelvin [55]. Temperature affects friction and fretting wear [54]. The fretting process is gradual, with the fretted component in state of equilibrium or quasi- equilibrium [56]. Mohrbacher *et al*. [57], Huq and Celis [58], and later Fouvry *et al.* [59, 60, 61, 62] developed an energy based model for fretting wear. Exhaustive measurements by these groups showed the Archard wear law, equation (4) to be an inappropriate descriptor of their data. Mohrbacher *et al*. [57] found that the wear volume, measured by measuring the geometry of the wear scar beneath the fretting contact, when plotted versus total friction energy dissipated, produced a straight line. This observation was confirmed by others [59, 60, 61, 62, 58, 63, 64] for fretting wear of various coatings on substrates. Models of fretting wear, when based on accumulated friction energy dissipated [65, 66, 62, 67], can predict the time evolution of the wear scar profile. The principal dissipation modes for fretting wear are plastic deformation and adhesion. This is sometimes supplemented by corrosion and oxidation.

Bryant, Khonsari and Ling's [68] application of the Degradation-Entropy Generation theorem to fretting wear predicted a dependence on friction energy dissipated, consistent with exhaustive measurements of Huq and Celis [58], Fouvry *et al.* [59, 60, 61, 62], and Mall *et al.* [63, 64], who collectively found Archard's wear law to be a poor predictor of fretting wear. Fretting wear involves an irreversible process in a critically stable state near equilibrium, but in the process of transitioning to a new equilibrium state [56]. Instead of assuming a steady process or an equilibrium process, Bryant, Khonsari and Ling [68] used Dai *et al.*'s [56] thermodynamic condition, which perturbed about the equilibrium point, set the first

variation of entropy to zero, and expressed the system state in terms of the second variation.

## 3.4. Corrosion wear

Corrosive wear is a mechanism wherein a corrosion [69] film forms on the surface of a slider, and subsequent sliding removes the film. Removal of the film exposes underlying parent material to new corrosion. Oxidational wear is a form of corrosive wear [70, 71], especially in steels. The corrosion film, of different composition from the slider's parent material, has different mechanical behavior. Friction, hardness, and resistance to wear can change, depending on conditions. Corrosion films tend to protect underlying parent material from environmental and mechanical duress. For example, oxide films on aluminum discourage further surface oxidation [26, 69]. If the film has sufficient mechanical strength to not fail under stress imposed by sliding, the film and corrosion can reduce wear. Mechanically weak films, with low shear strength, can easily scale or flake off, and increase wear. Corrosive wear can involve mechanisms of adhesive, abrasive, and delamination wear. As with any reaction, surface corrosion is controlled by supply of reactants and activation energy. Reactant supply is controlled by oxygen pressure (which controls oxygen concentration), and diffusion of metal ions and oxygen to the metal-corrosion film interface [69, 70]. The reaction rate affects the wear rate through the thickness and composition of the film. Friction heat can supply energy to drive reactions and encourage thicker films. Temperature influences composition, phase, and thickness of the surface oxide film. Thermodynamic conditions determine the corrosion reaction rate and products, which indirectly influences wear. Tendency to corrode is controlled by Gibbs free energy, which drives the direction of a reaction.

## 3.5. Fatigue wear

Fatigue wear is a process wherein repeated application of subcritical stress – stresses below the failure limit or material strength – moves dislocations through the stressed body, until they pile up and initiate tiny cracks. Continued application of the stress causes the cracks to propagate, or extend. After hundreds to possibly hundreds of millions of cycles of the repeated stress, a volume of material defined by the crack propagation path detaches from the body, forming a wear particle. Delamination wear [13] involves subsurface cracks a millimeter or so beneath the surface, propagating parallel to the surface, and driven by repeated passing of contact loads. Under repeated application of the load, the cracks propagate until, upon reaching a critical length, the cracks propagate up towards the surface. When the cracks intersect with the surface, strips peel off or delaminate from the surface. Pitting wear, a result of

rolling contact fatigue, is a fatigue process wherein cracks form under repeated application of rolling loads, usually associated with rolling element bearings or gear teeth contacts. Cracks initiate near or at the surface, and propagate into the material body at angles of about $20^{\circ}$ to the contact surface, opposite the rolling direction. As the cracks lengthen, the crack propagates parallel to the surface. Eventually, the crack propagation direction turns, and the crack intersects the surface, resulting in an arrowhead shaped wear particle with a concomitant pit in the surface.

### 3.6. Thermal and thermomechanical effects on wear

Thermal effects can accelerate wear and cause severe surface damage. Rubbing of bodies dissipates heat power $Q = Fv$ from friction force $F$ and relative velocity (e.g, slip velocity) between surfaces $v$. Friction heat can exert many different effects on sliders and lubricants. Higher temperatures can change material phase, which alters material properties. For example, metals can soften or melt, carbon graphite mixtures can harden, and thermal and electrical conductivities tend to diminish. Often, these altered properties reduce heat transfer from hot regions. Concentrated contact, called thermoelastic instability, hot spotting, thermal mounding, or thermal distress, is a thermomechanical instability that results in much higher wear. Rough surfaces segment the contact into discrete islands of contact within the apparent area of contact. As sliding commences, friction dissipation, which occurs at the islands of contact, is concentrated. Resulting elevated temperatures expand the regions about the contact islands, causing the spots to expand and grow outward toward the interface. Differences in spot geometry, contact pressure, and local friction cause some spots to heat and grow faster, which tends to separate lesser growing spots. The loads carried by the lesser spots transfer to the still-connected spots, inducing more intense conditions (forces, heating, temperatures, and thermal expansions) on the still-connected spots. This process continues until the slider runs on only a few spots, with temperatures of several hundreds to thousands of degrees kelvin and stresses at plastic limits. Under these extreme conditions, wear coefficients can double or increase tenfold or more.

## 4. Unifying friction and wear

Friction and wear, manifestations of the same interfacial physics and dissipative processes, are intimately related. Non-conservative friction force dissipates power and generates irreversible entropy. Wear is surface degradation driven by interfacial dissipative processes, including those associated with friction. This

section considers the thermodynamics, energy, entropy, and dissipative processes related to friction and wear.

## 4.1. Godet's third body

A major advance towards unifying friction and wear was Godet's [16, 53] introduction of the third body concept, which considers the "other" material entrapped within the interface between two sliding first bodies. The third body consists of contaminants and particles from the environment, material and wear debris shed from the first bodies, and films on the first body surfaces [4]. For sliding, a difference in velocities must exist between the bodies, which seems to create a discontinuity in velocity across the interface. Godet [16, 53] questioned the existence of this discontinuity, and suggested that material within the interface – the third body – must accommodate the discontinuity. Godet likened the third body's velocity accommodation effect to a lubricant film between two surfaces sheared by relative tangential motions. Here the flow velocities vary continuously across the film to accommodate the slip velocity across the bodies. To accommodate the discontinuous slip between sliding first bodies, Godet [16] showed that the third body must experience severe strains imposed by intense shear and compression during sliding.

The third body can serve as a media to transmit forces and prevent contact between first bodies. Since velocity accommodation subjects the third body to severe strains, the third body is a principal site of intense energy dissipation such as plastic work. Iordanoff *et al.*'s [72, 73] computer model of third body effects and kinematics suggested that the third body can behave like a fluid or solid. Flow of third body material influences friction and wear. Friction force, increased particle size due to clumping of particles, density of third body material, and third body and surface flows were found dependent on the amount of adhesion between small particles within the third body. Richard *et al.*'s [74] 3D simulations assumed sliding first bodies to be rigid, single layers of particles and third body particles to be 5 micron radius spheres. From particle motions driven by first body motions, macroscopic friction and rheology of the third body were derived. The model varied adhesion between particles and only allowed dissipation in the third body. Under different regimes of adhesion force, Richard observed four possible flow patterns of third body particles: fluid-like, with easy shear and mixing between particles; semifluidic, with some shear and mixing, but also with some particles moving in groups; elasto-plastic, with some particles moving only slightly, but others moving in groups with irreversible displacements; and elastic, with reversible motions and deformations. Richard found the dynamic friction coefficient proportional to the power dissipated. Experiments with many sub-

millimeter sized balls sheared between tangentially moving parallel plates verified their particle kinematics.

Iordanoff *et al.* [72] reviewed constitutive laws of third bodies, identified kinematic modes of third body particles for velocity accommodation, and surveyed possible fluid-like rheological constitutive models to describe third body behavior under imposed boundary conditions. Jang and Khonsari [75] treated powder lubrication as a granular media, formulated equivalent continuity, momentum, and energy equations into an equivalent Reynold's equation relating solid lubricant "pressure" to film thickness, and applied boundary conditions relevant to bearings to describe composite behavior of solid particles entrapped between sliders. Solid lubricants, a form of granular media subject to laws of thermodynamics [76], are a site of energy dissipation, including adhesion and plastic deformations. Particle to particle interactions manifest equivalents of temperature, pressure, and other thermodynamic states. Terrell and Higgs' [77] model of the motions of particles in abrasive slurries for chemo-mechanical polishing of silicon wafers considered the slurry dilute, to decouple the fluid pressures and flow (described by Reynold's equation) from particle motions.

The third body can be considered a principal locus of dissipative processes and entropy production associated with sliding. The literature sampled above suggests that sliding subjects third body material and particles to intense loads, strains, severe plastic deformation [4], and mixing. In addition, Singer [78] identified film formation and mixing or recycling of interfacial material and wear debris as important dissipative processes associated with third bodies.

## 4.2. Energy considerations for friction and wear

Friction and wear are related through energy dissipated by dissipative processes. Rymuza [79] considered friction as an energy transformation process: "Friction is a process that transforms the external mechanical energy to the energy of internal processes. The synergism of processes during friction leading to formation of dissipative structures is a characteristic feature of tribological systems." Rymuza's [79] proposed coefficient of "friction energy losses," the ratio of dissipated energy to input energy, reflects friction's dissipative nature. Rearrangement and disordering of material structures by work of dissipative irreversible processes causes wear. Friction force usually provides the energy for wear, although other sources can contribute, such as electrical dissipation during sliding wear of electrical brushes [80, 81]. Past models of wear reflected this energy dependence, albeit implicitly. Early models [9] related sliding wear in brakes as a ratio $J_\omega = w/W$ of wear volume lost w to work $W = FL$ of friction force $F$, where $L$ is distance slid. Note the similarity to equation (5). Another energy

related approach, *Pv* factor [17] with dimensions of power per unit surface area, implicitly describes friction power dissipation. Here *P* is the nominal pressure or load per projected bearing area, and *v* is the tangential component of velocity between the bearing surfaces. Some models employ *Pv* factor to predict wear, especially plastics [2]. Significant wear of boundary lubricated bearing surfaces can occur if a limit on *Pv* factor is exceeded [2]. *Pv* factor can predict wear of carbon brushes [81, 82]. Bayer [2] mentions that wear of cutting tools can be modeled with *Pv* factor. Several authors believe *Pv* factor appeared in their wear models because friction heating induces high temperatures that influence material response and wear. Material removal rate, which is surface recession per unit time, is proportional to *Pv* factor [83] for chemo-mechanical polishing of silicon wafers. This relation for abrasive wear [3] was first discovered by Preston. Ramalho reviewed energy dissipation methods for wear [84] and showed these methods could predict sliding wear, in addition to fretting wear. Several authors [56, 62, 59, 57, 64] showed fretting wear of oscillating contacts roughly proportional to the energy dissipated by friction force. Larbi *et al.* [85] related wear of steels to friction energy dissipated, for adhesive, abrasive, and oxidative wear. In a recent review, Briscoe and Sinha [86] identified many factors that influence polymer wear, all involved through dissipative processes.

Equation (5) suggests that wear should depend on the amount of friction energy dissipated. Uetz and Fohl [87] and Scherge *et al.* [88] noted that wear is driven by dissipation of friction, and proposed an energy balance to predict wear. Shakhvorostov *et al.* [89] monitored wear, friction, and bulk temperature for oil lubricated sliding of steel pins on a cast iron bushing, and split the power dissipated into heat carried by conduction, material lost by wear, and material transformations [88] near the surface. The amount of wear depended on the energy dissipated. Abdel-Aal [90, 91] concluded that wear aids dispersal of thermal energy dissipated by friction, since materials have limits on rate of dissipation of externally applied energy. Abdel-Aal found that the amount of wear correlated to the amount of energy dispersed, dispersal was temperature dependent, and transitions in wear rate and mechanisms depended on heat dissipation. Abdel-Aal constructed heat dissipation capacity (HDC) and specific rate of heat dissipation (SRHD) to measure heat dissipation ability. Wear rate of steels and other alloys correlated to these measures. Abdel-Aal reasoned that failure involved thermal distress from buildup of heat at the rubbing interface, and mentioned that his measures were related to entropy flow and entropy generation.

## 4.3. Thermodynamics of friction and wear

A thermodynamic analysis of a system focuses on exchanges of energy, entropy, and materials across the boundary of a control volume, which encloses a body of interest. A thermodynamic analysis captures the physics within the control volume, through an approach that applies conservation laws over the control volume. Because the perspective is global, a complete description of the microscopic physics occurring within the control volume is not necessary to predict system behavior, and can even be ignored. This is especially convenient when modeling systems with physics on microscopic to molecular length scales, but with effects that manifest on macroscopic length scales. Thermodynamic approaches have explained behavior of gases, liquids and solids. Since tribology has physics that occur over length scales from nanometers to millimeters, with concomitant effects that manifest on length scales from microns to meters [21] in components such as bearings, gears, brakes, and seals, a thermodynamic approach can be useful. In a series of papers Klamecki [92, 93, 94, 95] applied the laws of thermodynamics to a body undergoing wear. Klamecki [92] considered the entropy production during wear, and how the second law constrained wear. Entropy production consisted of components due to material deformation, mass loss, surface creation, and heat transfer. Klamecki [93] showed that mechanical friction interactions must be caused by dissipative processes, and assessed the entropy produced by friction about equilibrium states. In [94], Klamecki thermodynamically analyzed a sliding situation, to assess stability and entropy generation. Klamecki [95] considered sliding of metals, the work dissipated by plastic deformation about the sliding interface, and the entropy produced. In a three part paper, Zmitrowicz [96, 97, 98] applied Rational Thermodynamics [99, 100] to formulate governing equations for two bodies in sliding contact with a third body [16] in the interface. Rational Thermodynamics insures equations are consistent with conservation laws of physics and laws and assumptions of thermodynamics. The first paper [96] developed conservation equations – mass, momentum, angular momentum, energy, and entropy – for two bodies in contact with an interfacial layer or third body in between. Boundary constraints (conditions) imposed by contact between bodies were also formulated. Zmitrowicz then [97] considered constitutive laws governing behavior of materials of the sliding bodies and the interfacial layer or third body, and especially rules governing thermoelastic deformation and heat transfer over sliding contacts. Here the second law and nonnegative entropy restricted signs of material constants. Zmitrowicz finally [98] formulated constitutive laws for friction force, generation of friction heat, wear, and conduction of heat through contacts and third bodies. Again the second law

insured material constants and constitutive relations consistent with thermodynamics.

Thermodynamics is underpinned by conservation laws and balance statements. The first law of thermodynamics

$$dE = dQ - dW + \sum_k \eta_k dN_k \tag{6}$$

balances energy changes over a control volume. Here $dE$ refers to changes in internal energy, $dQ$ refers to heat transfer over the control volume (conduction and radiation) not involving transport of matter, $dN_k$ refers to change of mole number or molar mass $N_k$ (measured in moles) of species $k$, and $-dW$ accounts for work done on the environment by the control volume. Increments of work

$$dW = PdV + d\overline{W} = PdV + \sum_j F_j d\xi_j \tag{7}$$

involves products of generalized forces $F_j$ and generalized displacements $\xi_j$, and contributions from changes in volume $V$ induced by pressure $P$. Equation (6) also involves the chemical potentials for mass species $k$,

$$\eta_k = \frac{\partial E}{\partial N_k} \tag{8}$$

where the partial derivatives holds all independent variables except $N_k$ constant. Other definitions of chemical potentials replace $E$ in equation (8) with the other thermodynamic energies, such as Gibbs free energy $G$, see equations (13). Change of mole number $N_k$, expressed as

$$dN_k = dN_k' + dN_k^e \tag{9}$$

balances increments of molar mass $dN_k^e$ exchanged across the control volume, with increments $dN_k'$ created or consumed as products or reactants by reactions inside the control volume. The second law of thermodynamics [101]

$$0 \leq dS' = dS - dS^e \tag{10}$$

equates changes of entropy $dS$ within a control volume to entropy flow $dS^e$ exchanged across the control volume and to production of irreversible entropy $dS'$ by dissipative processes inside the control volume. The second law, equation (10), also demands non-negative production of irreversible entropy $dS'$. Equality in

equation (10) is restricted to reversible exchange of heat across the control volume, wherein entropy production $dS'$ is zero. The entropy flow term

$$dS^e = \frac{dQ + \sum \eta_k dN_k^e}{T} \tag{11}$$

accounts for entropy transported across the control volume by heat and mass flows. In the absence of mass flow ($dN_k^e = 0$) such as for a closed system, $dS^e = dQ/T$. Substituting equations (9) and (7) into equation (6), grouping and substituting in that result according to equation (11), applying equation (10) to the overall result, and finally expressing derivatives in terms of time $t$ yields

$$T\frac{dS'}{dt} = T\frac{dS}{dt} - \frac{dE}{dt} - \frac{d\bar{W}}{dt} - P\frac{dV}{dt} + \sum \eta_k \frac{dN_k'}{dt} \tag{12}$$

Equation (12) gives the irreversible entropy produced by a dissipative process operating at temperature $T$. The left side of equation (12), and thus the right side, is non negative. With solids and fluids, the internal energy $E$ is often replaced with enthalpy $H$, Helmholtz free energy $\Phi$, or Gibbs free energy $G$ as follows:

$$H = E + PV, \quad \Phi = E - TS, \quad G = E - TS + PV \tag{13}$$

Equations (6)-(7), (9), (10), and (11) contain sixteen variables $E$, $Q$, $W$, $\bar{W}$, $\eta_k$, $N_k$, $N_k'$, $N_k^e$, $S$, $S'$, $S_e$, $T$, $P$, $V$, $F_j$, and $\xi_j$. An equation of state for the relevant thermodynamic energy (e.g., $E = E\ (S, V, N_k, \xi_j)$) supplies differential relations that render constitutive laws for $\eta_k$, $P$, $T$, and $F_j$. Equation (8) for the chemical potentials is an example. Boundary conditions for heat $Q$ (as a temperature or heat flux condition), work $\bar{W}$ (as a displacement $\xi_j$ or force $F$ condition), volume $V$, and mass flow $N_e$ generate four conditions. The stoichiometry of chemical reactions, see equation (32), generates conditions for $dN_k'$. Overall, the variables exceed the number of equations by two, requiring two more conditions for closure. The system's dynamic state can impose conditions on the relevant thermodynamic energy and system entropy. Classical irreversible thermodynamics [102, 99] deals with systems at or near equilibrium, or at steady state. At equilibrium, entropy $S$ maximizes and production of entropy ceases ($dS' = 0$). At a steady state, changes in entropy and energy over the control volume vanish, fulfilled by

$$dE = 0, \quad dS = 0 \tag{14}$$

Tribology involves systems not in equilibrium with motion and energy at the interface. However, many tribology systems can be considered near equilibrium, or operating at steady state. Many sliding devices running at a steady speed can be approximated as steady state, without large error in analysis [103]. Fretting and fretting wear involves low frequency oscillating motions, with stable slowly varying temperatures [55], suggesting a system near equilibrium. Here the entropy and relevant thermodynamic energy [101] can be expanded via a Taylor series about the equilibrium point $S_e$. For example

$$\Delta S = S - S_e = \delta S + \frac{1}{2}\delta^2 S + \cdots \tag{15}$$

With the equilibrium condition, equation (14), applied to the first order term, $\delta S = 0$, the higher order terms in equation (15) govern behavior. Dai Zhendong *et al.* [56] treated fretting wear as an irreversible process in a critically stable state near equilibrium, in the process of transitioning to a new equilibrium state. Dai predicted changes induced by fretting using values for states near the local equilibrium point, obtained through the second order term in equation (15). For continuums, equations (6) to (15) have continuum counterparts [99, 96, 97, 98].

Friction force and wear manifest from irreversible dissipative processes

$$p_j = p_j(\zeta_k^j), \quad \zeta_k^j = \zeta_k^j(t) \tag{16}$$

operative at the sliding interface. These processes transform work into heat, and generate entropy. Here $j$ indexes the process energy $p_j$, which depends on a set of time dependent phenomenological variables $\zeta_k^j$ indexed by $k$. For example, fracture driven by friction force draws energy to form new crack surface, and materials sheared between sliding surfaces derive energy from friction force. Degradation is a consequence of dissipative irreversible processes that disorder a system. The dissipative processes can be directly linked to thermodynamic entropy, or associated thermodynamic energies. Feinberg and Widom [104, 105] related material or component parameter degradation to Gibbs free energy, and predicted change in the system characteristic results with a log-time aging behavior versus time. The emerging field of damage mechanics [106] constructs a "damage parameter," but also tracks entropy and thermodynamic energies [107, 106], to obtain closure of the physics equations needed to numerically estimate damage. Entropy can quantify the behavior of irreversible tribological processes such as friction and wear [92, 93, 94, 95, 96, 97, 98]. The amount of fretting wear of specimens in oscillating fretted contacts was shown [56, 62, 59, 57, 64] roughly proportional to the energy dissipated by friction force. To treat fretting wear, Dai

Zhendong *et al.* [56] equated the perturbed entropy flow to the perturbed entropy production, and solved for wear as the mass flux component of entropy flow. Doelling *et al.* [103] proposed a thermodynamic degradation paradigm, wherein degradation by wear under boundary lubricated conditions was related to the entropy generated during sliding. Later, Ling, Bryant and Doelling [108] analyzed the irreversible entropy produced by sliding, for application to wear.

To relate degradation to entropy production, Bryant, Khonsari and Ling [68] formulated and proved a "Degradation-Entropy Generation" theorem (DEG theorem), applicable to a generalized material degradation. Concomitant with material degradation, the second law of thermodynamics, equation (10), asserts that irreversible entropy $dS'$ must be produced. The irreversible entropy produced, and the associated degradation must both depend upon the same dissipative processes $p_j = p_j(\zeta_k^j)$ and phenomenological variables $\zeta_k^j$. The theorem relates degradation $w$ to the irreversible entropy $S_j'$ generated by the array $p_j$ of dissipative processes. Application of the chain rule yields the rate of entropy generation

$$\frac{dS'}{dt} = \sum_{j,k}\left(\frac{\partial S'}{\partial p_j}\frac{\partial p_j}{\partial \zeta_k^j}\right)\frac{d\zeta_k^j}{dt} = \sum_j \frac{dS_j'}{dt} = \sum_{j,k} X_k^j J_k^j \tag{17}$$

expressed as a sum of products of generalized thermodynamic forces $X_k^j = (\partial S'/\partial p_j)(\partial p_j/\partial \zeta_k^j)$ and generalized thermodynamics fluxes or flow $J_k^j = d\zeta_k^j/dt$. Index $j$ indicates individual dissipative processes, and the sum over $j$ accumulates the entropy generated by the array of processes. Notation $\sum_{j,k}$ indicates a double sum. The term $\partial S'/\partial p_j = 1/T_j$ in $X_k^j$ was recognized as the inverse of a temperature $T_j$ related to $p_j$, suggesting that $F_k^j = \partial p_j/\partial \zeta_k^j$ is a generalized force conjugate to the generalized flow $J_k^j = d\zeta_k^j/dt$, an energy concept from system dynamics [6, 7]. By recognizing that degradation and entropy generation *must depend on the same dissipative processes and phenomenological variables* through the dissipative processes, again using the chain rule, Bryant *et al.* [68] expressed the rate of degradation

$$\frac{dw}{dt} = \sum_{j,k}\left(\frac{\partial w}{\partial p_j}\frac{\partial p_j}{\partial \zeta_k^j}\right)\frac{d\zeta_k^j}{dt} = \sum_{j,k}\frac{\partial w/\partial p_j}{\partial S'/\partial p_j}\left(\frac{\partial S'}{\partial p_j}\frac{\partial p_j}{\partial \zeta_k^j}\right)\frac{d\zeta_k^j}{dt} = \sum_{j,k} B_j X_k^j J_k^j = \sum_{j,k} Y_k^j J_k^j = \sum_j B_j \frac{dS_j'}{dt} \tag{18}$$

as products of generalized degradation forces $Y_k^j = (\partial w/\partial p_j)(\partial p_j/\partial \zeta_k^j)$ and the same $J_k^j$ as in equation (17). The outer equalities equate the degradation rate *dw/dt* to a linear combination of the rates of entropy production $dS_j'/dt$ of each of the dissipative processes $p_j$. In equation (18), the degradation coefficient

$$B_j = \frac{\partial w/\partial p_j}{\partial S'/\partial p_j} = \left.\frac{dw}{dS'}\right|_j \tag{19}$$

is a material property which, like other material properties, must be measured. The notation $|_j$ indicates that the right side of equation (19) must be measured with dissipative process $j$ active. Although equation (17) is written in the form of the entropy generation formula of classical irreversible thermodynamics, limited to near-equilibrium and stationary thermodynamic processes [102], the theorem proof [68] expressed degradation and entropy generation in terms of the partial derivative $X_k^j$, $J_k^j$ and $Y_k^j$, and made no assumptions on the thermodynamic state. Thus the theorem is also valid for processes far from equilibrium, the purview of Extended Irreversible Thermodynamics [100].

## Wear

By enclosing the sliding surface and near surface regions of a wearing body with a tribological control volume, as shown in figure 1, Bryant *et al.* [68] then applied the DEG theorem to sliding wear and fretting wear, induced by friction force.

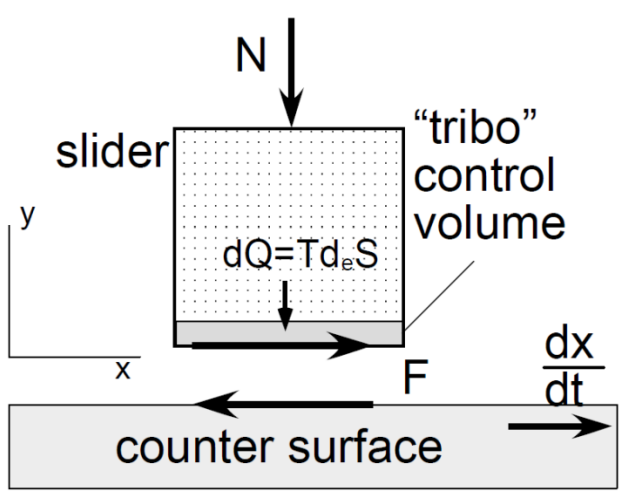


**Figure 1.** Thermodynamic analysis of slider on counter-surface, with tribo control volume.

Equation (17) was applied to the power dissipated by friction force $F$. The theorem [68] resulted in a thermodynamic based derivation of the Archard-Holm wear law (4). Sliding wear at steady speed $v = dx/dt$, driven by friction force $F$, was treated as a stationary thermodynamic process, wherein $dS = dE = 0$, as in equation (14). In addition, the energy $\eta dN^e$ transported out of the control volume by wear debris was neglected in the first law, equation (6), compared to the work $-dW = Fdx$ and heat exchange $dQ$ terms. By applying equation (18) to the "tribo" control volume of figure 1, Bryant *et al.* [68] found thermodynamic force $X = F/T$, thermodynamic rate $J = dx/dt$, wear-degradation force $Y = BX$, and volumetric rate of wear per unit time to be

$$\frac{dw}{dt} = YJ = BXJ = B\frac{F}{T}\frac{dx}{dt} \tag{20}$$

Here $T$ is the temperature at the contact between the rubbing bodies. For convenience, subscripts and superscripts were dropped. For sliding of an insulated copper rider against a steel counter surface under boundary lubricated conditions, Doelling *et al.* [103] measured wear, friction and normal forces, and temperatures at and about the sliding surface. From the temperatures was derived entropy flow $dS^e/dt$. Because the sliding system is steady, the entropy flow equated to the entropy generated $dS' = Fdx/T$ in the "tribo" control volume. From measurements of slider wear $w$ arose estimates of slope $dw/dS'$, which is degradation coefficient B in equation (19). By comparing equation (20) to equation (4), Bryant *et al.* [68] related the wear coefficient $K = B\mu H/T$ to the degradation coefficient $B$, contact temperature $T$, friction coefficient $\mu$, and hardness $H$ of the wearing body. The wear coefficient thus calculated compared to within one to two percent of wear coefficients measured by Rabinowicz [48], under same conditions. Of interest is that Rabinowicz's wear coefficient $K = 10^{-4}$, calculated via equation (4), arose from measurements of wear, forces and distance, whereas Doelling *et al.* [103] obtained the wear coefficient from measurements of wear and temperatures. The theorem also predicted the empirically observed dependence of fretting wear on friction energy dissipated in fretted specimens [62, 59, 57, 64]. Following Dai *et al.* [56], this formulation treated fretting wear as an irreversible thermodynamic process, in a critically stable state near equilibrium, but in the process of transitioning to a new equilibrium state. The formulations were similar to equations (17) through (20), except that the term $Fdx/dt$ in equation (20), the product of power conjugates $F$ and $dx/dt$ [6, 7], was identified as the rate of work $dW/dt$ dissipated in the fretted contact, similar to equation (5).

The theorem formulates degradation (and wear as a special case) in terms of the dissipative processes associated with the sliding interface, and suggests a

form for the generalized force $F_k^j = \partial p_j / \partial \zeta_k^j$. When the dissipative process $p_j$ is mechanical, $F_k^j$ contributes a component to friction force, consistent with equation (2). Consistent with equation (3), equation (18) suggests that total wear is the sum of components from different mechanisms. These components can be related to the dissipative processes $p_j$ germane to the mechanisms, via the energetics embedded in the process entropy generation terms $dS_j'/dt$. In equation (18), $dS_j'/dt$ acts as an "influence function" and brings the influence of the dynamics of process $p_j$ to the degradation wear rate. Because entropy generation $dS_j'/dt$ of dissipative processes $p_j$ appears important, the next section will review principal dissipative processes associated with friction and wear, and concomitant entropy generation.

## Friction force

This section relates friction force to the dissipative processes at the sliding interface that manifest friction force. Recall that equation (12), an amalgam of the first and second laws, balances entropy production with the dissipation from work crossing the tribological control volume, and changes in thermodynamic states. With rate of external work $-d\overline{W}/dt = F\upsilon + N\dot{\alpha}$ arising from friction force $F$ and sliding velocity $\upsilon$, and normal force $N$ and rate of normal approach $\dot{\alpha}$ between surfaces, equation (12) gives

$$T\dot{S} - \dot{E} + F\upsilon + N\dot{\alpha} - P\dot{V} + \sum \eta_k \dot{N}_k' = T \sum_j \dot{S}_j' \geq 0 \tag{21}$$

where "dot" denotes time derivative. Equation (21) relates the power dissipated by contact forces to entropy production and change of states. The nonnegative entropy production asserted by equation (21), along with independence of $v$ from $\dot{\alpha}$, demands constancy of direction between friction force $F$ and sliding velocity $v$. If expressions describing the entropy produced by the various dissipative processes are substituted into the right side, friction force can be estimated. To simplify the formulation, and to stress the connection of friction to dissipative processes, assume steady sliding conditions (see equations (14)), no reactions or negligible influence of reaction energy on friction force, and interfacial compressions principally due to normal force, i.e., $N\dot{\alpha} \approx P\dot{V}$. Equation (21) then simplifies to

$$F \approx \frac{T}{\upsilon} \sum_j \dot{S}_j' \tag{22}$$

Similar to equation (2), the total friction force results from a sum over friction components arising from various dissipative mechanisms operative at the sliding interface. Understanding and quantitatively describing the entropy produced by these processes or mechanisms is germane towards understanding and modeling friction. Equation (22) suggests that a quantitative description of friction force can be based on the entropy production by the associated dissipative friction mechanisms. This is also true for wear, as equations (18) and (20) suggest. Describing the entropy produced by the various dissipative processes operative at a sliding interface is the purview of the next sections.

## 4.4. Dissipative processes of friction and wear

Almost all processes of nature are dissipative and irreversible. Friction force is the macroscopic manifestation of dissipative processes operating on molecular to micron scales [109]. A fundamental question is *how* the organized motion of bodies, including their surface atoms, transform into the disordered thermal motions of atoms characteristic of irreversible adhesive friction. Starting in the 1990s, many investigations of the dissipative processes and mechanisms of friction have been conducted [109, 110, 111, 112]. These dissipative processes include phenomena such as conversions [110], irreversible losses due to adhesion [21, 112], plastic deformation and mechanisms in metals [113, 114], and motions of molecular chains adhered to surfaces, during collisions between chains caused by sliding [115]. Discussed in this section are dissipative processes prominent to tribology, and the associated entropy generation. Nosonovsky [15] mentions that tribological processes are in principle reversible, but become irreversible and dissipative due to hysteresis mechanisms caused by differences in length scales of the forward and reverse segments of the mechanism. Straffelini [28] extended the thermodynamic work of adhesion, plastic deformation, and other irreversible effects such as back transfer of material within a sliding contact, and showed coefficient of friction dependent on thermodynamic work of adhesion.

### 4.4.1. Adhesion

Adhesion is a hodgepodge of many types of bonding forces [15] operating on microscopic scales. Although these microscopic forces are in principle reversible, many factors cause adhesion to be irreversible and dissipative. Singer [109] and Krim [111] observed that friction due to adhesion usually involves dissipative processes operating on nano to atomic length scales. Pure van der Waals interactions between individual molecules are reversible, however, in large groups, motions of molecules during surface separation can couple to other allowed

vibration modes. Since the sequence of motions that originally joined the surfaces do not play backwards, the "acoustic loss" [21] process becomes irreversible. Hirano [112] formulated dissipation due to friction in terms of atomic potentials between contacting surfaces, and explained static friction force via "atomistic locking" of surfaces. Dynamic friction force was explained via movement of atoms on the surfaces, wherein kinetic energy of the slider, upon separation of interacting atoms of opposing surfaces, transfers to translational vibration modes of surface atoms. These phonon vibrations can couple into other modes associated with internal degrees of freedom. Since even a small surface has trillions of atoms, each with many internal degrees of freedom, Hirano concluded this diffusion to be irreversible, since the probability of backup of energy through the various modes into the original motion is nil. This dissipative process can also permanently displace atoms from old equilibrium positions to new positions, altering the material structure. With simple models, Streator [116] demonstrated dynamic instabilities that coupled friction power into heat loss. Harrison and Perry [115] studied friction dissipation mechanisms for boundary lubricated sliding. Nosonovsky [15] proposed a hysteresis mechanism for adhesion, wherein a dissymmetry occurs between joining and in separating of adhesion forces during sliding.

Classical theory of adhesion [20] defines an interface surface energy $\gamma$ as the work per unit area to create new surface area. The energy of two solid bodies in contact over an area $A$ is $E_c = E_o + \gamma_{12}A$, where $\gamma_{12}$ is the surface energy of the interface and $E_o$ is the baseline energy. After separating the surfaces, the energy of the two solids is $E_s = E_o + \gamma_1 A + \gamma_2 A$, where $\gamma_1$ and $\gamma_2$ are the surface energies to create and isolate the new free surfaces 1 and 2. To separate the two surfaces, work $W_{sc} = E_s - E_c$ must be expended. The energy per unit area to separate the surfaces is

$$\gamma = \frac{W_{sc}}{A} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{23}$$

Surface energies of 1 to 3 J m$^{-2}$ are observed for clean metals, 0.1 to 0.5 J m$^{-2}$ for ionic crystal ceramics, and less than 0.1 J m$^{-2}$ for molecular crystals and polymers [20]. When two solids join and form a single crystal, $\gamma_{12} = 0$, and $\gamma_1 = \gamma_2 = \gamma_o$, giving $\gamma = 2\gamma_o$. Considering equations (12), (13), and (23) under isothermal conditions, the entropy generated by separating the surfaces against the forces of adhesion can be estimated as

$$\Delta S_s' = \frac{\gamma}{T} A_s \tag{24}$$

where $T$ is the local temperature of the media, and $A_s$ is the amount of free surface produced. The separation work $W_{sc}$ in equation (23) originates from free energy, see equation (13), from work crossing the system boundary $dW$, from changes in the free energy $d\Phi$, or combinations thereof.

### 4.4.2. Plastic deformation and viscous dissipation

For dry or poorly lubricated sliding of metals, a major portion of the work dissipated by rubbing involves plastic deformation [95] and related dissipative effects [110]. The energy dissipated by plastic deformation is a major contributor to friction force [114]. Plastic flow in ductile metals occurs when the metal is overloaded in shear. Motions of dislocations drastically reduce the loads needed to cause permanent deformation [117, 118, 13]. Sliding imposes tractions onto the sliding surfaces, which can subject the sliding bodies and interfacial third body material to intense shears. Plastic deformation occurs through large surface and subsurface plastic deformation imposed by surface tractions, and surface plowing [13] observed during abrasion and asperity deformation.

For copper sliding against steel, Tsuya [119] observed intense plastic deformations in a 10 to 50 $\mu$m thick skin layer on the softer copper, and attributed the plastic dissipation in this "severely deformed region" as a principal mechanism of friction force. Rigney *et al.* [113, 120, 114] and Heilmann and Rigney [121] equated the friction energy to the plastic work dissipated, in good agreement with Tsuya's measured friction force. Kennedy [122] measured near-surface deformations due to sliding, using microscopic observation of the contact region, and compared these values with finite element viscoplastic estimates of the high rate plastic strains of a moving contact. Kennedy suggested the thickness of the severely deformed region was less than 300 $\mu$m, for the loads in his experiment.

For metals, plastic dissipation transforms the material state and structure in the near surface regions about the asperities. Dislocations appear, move, and annihilate, effecting permanent change. Plowing removes and relocates material from one or both sliding bodies. Suh and Komvopoulos *et al.* [13, 29, 33, 32] macro and mesoscale observations identified plowing and concomitant plasticity as the dominant cause of friction and wear for sliding of metals. At smaller scales, Schmid measured forces during micro plowing of aluminum, with an atomic force microscope [123, 124, 125], and reached similar conclusions. After significant plastic flow, a mechanically mixed layer can develop within a wearing body [126], with sublayers atop the substrate that include mixed material, fragmentation, fracture, and flow. Material is usually under compression during sliding. Biswas [126] observed that instabilities within this layer governed transition to higher wear

rates. Instabilities can occur at different combinations of load and velocity, and appear to depend on temperature and strain rate.

The energy dissipated by large plastic deformation, and the entropy production can be obtained from the dissipation function of continuum mechanics [127]

$$\Upsilon = \int \sigma : \frac{d\epsilon}{dt} \approx \tau_f |\dot{\epsilon}^*{}_{\max}|, \quad dS' = \frac{\Upsilon}{T} \tag{25}$$

where $\sigma$ is the stress tensor, $d\epsilon/dt$ is the rate of strain tensor, and the colon denotes tensor product. The form of equation (25) is valid for solids and fluids. For plastic work dissipated in solids [118], $\sigma$ is associated with maximum shear, and can be approximated by the flow stress in shear $\tau_f$, defined as the true stress needed to maintain plastic deformation at a particular true shear strain $\varepsilon^*$. Theorems can supply upper and lower bounds to the plastic work [118], if the stress field or velocity fields, respectively are known.

For sliding of ductile metals on hard metals, power loss occurs mainly in the severely deformed region, via intense localized plastic work. Rigney [113] proposed a simple estimate $\Upsilon \approx \bar{E}(\omega hs)$ of the plastic work dissipated, where $\bar{E} \approx \tau\bar{\epsilon}$ is the average deformation energy dissipated per unit volume of the severely deformed region, $s$ is the distance slid, $h$ is the thickness of the region, and $\omega$ is the width of the sliding track. Within the severely deformed region, $\tau$ was estimated as the yield strength in shear, and $\bar{\epsilon}$ is the average strain in that region. Equation (25) suggests the entropy produced for steady sliding can be estimated as

$$dS' = \frac{\bar{E}(\omega hds)}{T} \tag{26}$$

### 4.4.3. Abrasion and cutting

Abrasion, associated with plowing and adhesion friction and abrasive wear, see section 3, cuts grooves into surfaces, which forms “chips” or wear particles. Here a cutting edge moves at a depth below the surface, and severs material. Cutting or machining of metals involves three dissipative events: (1) intense plastic deformation in a shear zone directly in front of the cutting edge, (2) adhesion of the chip—material severed from the work piece—to the cutting tool, and (3) plastic deformation and fracture of the chip as the chip flows off the cutting tool. The cutting tool contains the cutting edge, which moves through and cuts the work piece. Abrasion, a form of cutting, is characterized by several dissipative processes operating together. Specific cutting energy $u_s$ is the energy needed to machine a unit volume of material from a workpiece [128]. Specific cutting energy, measured for machining and grinding of most metals, implicitly lumps all the dissipative

processes associated with cutting of metals. Specific grinding energy $u_g$ measures the energy to grind a unit volume of material from a workpiece. Grinding is a machining process wherein very many small abrasive grains on a grinding wheel collectively cut and remove material from a workpiece. In addition to the dissipative processes of cutting, grinding and thus $u_g$ includes energy dissipated by fracture and wear of abrasive grains, and adhesive friction due to rubbing of the wheel's binding material against the workpiece. Since specific cutting or grinding energy represents the losses during cutting, the entropy produced per unit volume can be estimated by

$$\delta S' = \frac{u_i}{T} \tag{27}$$

where $u_i$ is the specific energy of grinding or cutting, depending on the conditions of the abrasion.

### 4.4.4. Fracture

Fracture is an irreversible process wherein material, continuous within a body, separates and forms new free surface. Bodies overstressed can fracture, especially brittle materials. A crack has crack tips that intensify stresses about the crack tips. These elevated stresses can rupture material, extending the crack. For a crack of length $a$ in a two dimensional (2D), linearly elastic brittle material at uniform temperature $T$, Rice [129] derived the irreversible entropy generated by the crack extending an amount $da$. Rice enclosed the cracked body with a control volume, formulated equation (12) in terms of Helmholtz free energy $\Phi$, see equation (13), for the special case of constant temperature, no material loss, and no chemical reactions or phase changes, and considered $\Phi(\Delta_k, a, T) = \mathrm{U}\ (\Delta_k, a) + 2\gamma_o a$ to consist of surface energy $2\gamma_o a$ and elastic strain energy $U = U\ (\Delta_k, a)$ dependent on the displacements $\Delta_k$ applied at the boundaries of the control volume, and the crack length $a$. Since Rice's formulation was 2D, all quantities were viewed on a per thickness basis. The work of isothermal separation of surfaces, see equation (23), involves the surface energy $\gamma = 2\gamma_o$ introduced in equation (23) of section 5.4.1. Since the summation terms in the incremental Helmholtz free energy $d\Phi = \sum_k (\partial U/\partial\Delta_k)d\Delta_k + (\partial U/\partial a)da$ equates to the work $-dW$ performed by forces $P_k = \partial U/\partial\Delta_k$ applied at the boundary, Rice solved for the entropy produced during crack extension as

$$\frac{dS'_{cr}}{dt} = \frac{G-2\gamma_o}{T_{cr}}\frac{da}{dt} \tag{28}$$

In equation (28), $G = -\partial U/\partial a$ is the energy release rate, $2\gamma_o$ is the reversible work of separating surfaces, per unit area, and $T_{cr}$ is the temperature of the cracked material at the crack tip. Equation (28), valid for 2D plane strain, can be extended to three dimensions (3D) by integrating the right side of equation (28) over the 3D curve through the material that defines the crack tip or crack front. Comparing equation (28) to equation (17) gives thermodynamic force $X = (G - 2\gamma_o)/T_{cr}$ and thermodynamic rate $J = da/dt$, for fracture. To apply equation (28) to tribological systems such as delamination wear or pitting, see sections 4.5 and 4.5, the strain energy $U$ must be expressed in terms of the loads applied to the cracked body.

### 4.4.5. Phase changes

Phase changes morph a material to another state or structure, which alters material properties and behavior, including tribological behavior. Energy is absorbed and entropy is generated by the change. Phase changes that can be induced by sliding include melting, solidification, recrystallization, and vaporization. With change of structure, material properties such as strength, elastic modulus, and conductivity can change, altering tribological behavior. The entropy generated by a phase change [101] is

$$\Delta S = \frac{\Delta H}{T_{phase}} \tag{29}$$

where $\Delta H$ is the change in enthalpy – the latent heat absorbed or shed during the phase change – and $T_{phase}$ is the temperature associated with the phase change. For transitions from solid to liquid, and vice versa, $T_{phase}$ is the melting temperature, and $\Delta H$ and $\Delta S$ are the molar enthalpy and molar entropy of fusion. For transitions from liquid to gas, $T_{phase}$ is the boiling temperature, and $\Delta H$ and $\Delta S$ are the molar enthalpy and molar entropy of vaporization. Solids can change material structures by transforming to a different crystal structure, for example, the iron changes from an alpha body centered cubic structure to the gamma face centered cubic structure at 914°. The entropy produced during a structural phase change is also given by equation (29). The rate of a phase change is governed by the reaction kinetics, which depends on the type of transformation.

### 4.4.6. Chemical reactions

Chemical reactions alter the composition of materials, which changes the material properties and tribological behavior of sliding bodies. Several forms of sliding wear involve chemical reactions and concomitant change of material

properties and behavior due to altered composition of interfacial components. During oxidational wear of steel [71], hardness of surface layers are reduced, which equation (4) suggests should alter wear rate. For a chemical reaction with stoichiometric equation

$$\sum_{i=1}^{m_r} \kappa_i R_i \rightarrow \sum_{j=1}^{m_p} \lambda_j P_j \tag{30}$$

involving reactants $R_i$, $i = 1, \ldots, m_r$, and products $P_j$, $j = 1, \ldots, m_p$, in stoichiometric proportions $\kappa_i$ and $\lambda_j$ , Kondepudi and Prigogine [101] give the entropy produced as

$$\frac{dS_r'}{dt} = \frac{A}{T}\frac{d\xi}{dt}, \qquad A = \sum_{i=1}^{m_r} \kappa_i \eta_i - \sum_{j=1}^{m_p} \lambda_j \eta_j \tag{31}$$

The chemical affinity $A$ for the reaction depends on the chemical potentials $\eta_k$ of reactants and products, see equation (8), and coefficients $\kappa_i$ and $\lambda_j$ in the stoichiometric equation (30). Reactants contribute positive terms to A and products contribute negative terms. Here $T$ is the temperature of the reaction. The extent of the reaction $\xi$ is defined such that

$$d\xi = \frac{dN_i'}{-\kappa_i} = \cdots = \frac{dN_j'}{\lambda_j} \tag{32}$$

where terms arising from reactants have negative signs, terms arising from products have plus signs, and the prime on the mole numbers $N_r'$ and $N_p'$ indicate changes in molar mass due to chemical reactions, see the text following equation (9). Comparing equation (31) to equation (17), thermodynamic rate $J = d\xi/dt$ and thermodynamic force $X = A/T$. If equation (30) is the resultant of several successive reaction steps, then the affinity of equation (31) is the resultant affinity, and equation (31) gives the entropy production if the temperature $T$ is maintained throughout the steps.

Formation of corrosion films on surfaces affect friction and wear [71]. Oxidation of copper to cuprous oxide, is a three step process that involves formation of copper ions, transfer of electrons to oxygen, and combination. For this reaction, stoichiometry $4\ Cu + O_2 \rightarrow 2\ Cu_2O$ summarizes the three step process, affinity $A = 2\eta_{Cu2}\ O - 4\eta_{Cu} - \eta O_2$, and, extent of reaction is $d\xi = -dN_{\mathrm{Cu}}'/4 = -dN_{\mathrm{O_2}}' = dN_{\mathrm{Cu_2O}}'/2$.

### 4.4.7. Diffusion

Diffusion migrates molecules, ions, or particles of a species from regions of higher concentration to regions of lower concentration. Diffusion is driven by concentration differences or gradients, which changes the thermodynamic state, thermodynamic energies, and chemical potentials, see equations (6), (13), and (8). For diffusion from region 1 of higher concentration, to region 2 of lower concentration, the mass gained by region 2 must equal the mass lost from region 1, i.e., $dN_2 = -dN_1$. For entropy generation, diffusion is viewed as a "reaction" [101], with material in regions of higher concentration being "reactants" and material transported to regions of lower concentration being "products". Rate of entropy production is then governed by equations (31) and (32), but with chemical potentials $\eta_1$ and $\eta_2$ principally determined by concentrations of species, and equation (32) defined by mass conservation. For diffusion, $T$ in equation (31) is the temperature of the diffusion media. For the simple example cited, equation (32) becomes $d\xi = dN_2 = -dN_1$, affinity of equation (31) becomes $A = \eta_1 - \eta_2$, and rate of entropy production $dS'/dt = [(\eta_1 - \eta_2)/T]d\xi/dt$.

### 4.4.8. Mixing of materials

When materials of initially separate but different species mix, entropy is generated in the less organized mixture. Mixing pertinent to tribology occurs principally in the third body or about the interface, see section 5.1, and can involve mixing of macroscopic solid particles and/or solution of solid or fluid constituents. For particles, the irreversible entropy produced when $n$ initially pure constituents having volumes $V_\alpha$, $\alpha = 1, 2, \ldots, n$ are mixed is the difference between the sum $S_i = \sum_{\alpha=1}^{n} S_\alpha$ of the entropies $S_\alpha$ of the initial states and the entropy $S_f$ of the final mixed state [130]

$$\delta S'_{mix} = S_f - S_i = \sum_{\alpha=1}^{n} kN_\alpha \ln \frac{V}{V_\alpha} \tag{33}$$

where $k = 1.38066\times10^{-23}$ J/K is Boltzmann's constant, $N_\alpha$ is the number of particles of species $\alpha$, and final volume $V$ contains the mixture. For liquids and gases, $V = \sum_{\alpha=1}^{n} V_\alpha$, but packing factors may be needed to estimate $V$ for solids or particles. Since $V/V_\alpha \geq 1$, the entropy produced is positive. Equation (33) was derived for mixing of ideal gases initially segregated into separate volumes, $V_\alpha$, but was extended by Muller and Weiss [130] to mixing of other pure "particles". For tribology, this could include third body debris, lubricant powders, or liquid dispersions. Derivation of equation (33) applied Boltzmann's formula $S = k\ln(\omega)$, where $\omega$ is the probability of occurrence of a

micro-state. Since the probability of a specific particle (e.g., gas molecule or wear particle) being in volume $V_\alpha$ – and not other parts of $V$ – is $V_\alpha/V$, the probability of $N_\alpha$ independent particles being in $V_\alpha$ is $\omega_\alpha = (V_\alpha/V)^{N\alpha}$. Boltzmann's formula renders $S_\alpha = kN_\alpha \ln(V/V_\alpha)$. The final fully mixed state, with very many micro-state manifestations and probability near unity, has vanishing $S_f$.

The molar entropy $\bar{S}'_{sol}$ of a solution of $n$ initially pure constituents, expressed in terms of molar fractions $x_\alpha = N_\alpha /N$, was presented in [101] as

$$\delta \bar{S}'_{sol} = -R \sum_{\alpha=1}^{n} x_\alpha \ln(x_\alpha) \tag{34}$$

where $R$ is the universal gas constant. Here $\bar{S}'_{sol}$ is the entropy produced per mole $N$. The ideal gas law suggests different gases at same temperature and pressure have same ratio of volume to number of moles, giving $x_\alpha \approx V_\alpha/V$. Multiplying and dividing the right side of equation (33) by Avogadro's number $N_o$, and dividing both sides by $N$ renders equation (34), since $R = kN_o$ and $N_\alpha = N_\alpha/N_o$.

The entropy production rates can be obtained from equations (33) and (34) by dividing those entropy differences by the time required for mixing.

### 4.4.9. Heat transfer

Transferring an amount of heat $dQ$ from a body at a higher temperature $T_h$ to a body at a lower temperature $T_l$ generates entropy. The entropy of the hotter body reduces by $dQ/T_h$, and the entropy of the cooler body increases by $dQ/T_l$. The system is isolated, giving entropy flow $dS^e = 0$ from the exterior. The entropy change is $dS = dQ/T_l$. Via equation (10), the entropy generated (in the cooler body) by the transfer of heat $dQ$ is

$$dS'_Q = dQ\left(\frac{1}{T_l} - \frac{1}{T_h}\right) \tag{35}$$

With reference to equation (18), $J = dQ/dt$ and $X = 1/T_l - 1/T_h$. Heat flows from regions of high to low temperature. For temperature differences $T_h - T_l$, Fourier heat conduction gives $J = dQ/dt = \beta(T_h - T_l)$, where $\beta = AK/\ell$ is the thermal conductance, consisting of thermal conductivity $K$, cross section area $A$, and length $\ell$.

## 5. Summary

Friction and wear mechanisms were reviewed, analyzed, and related in terms of their associated thermodynamics, and energy losses and entropy produced by

common dissipative processes. Friction force relates to the entropy generated by those dissipative processes, see equation (22). Wear rate was expressed by the Degradation-Entropy Generation theorem as a linear combination of entropy generation of the dissipative processes, for example see equations (18) and (20). Dissipative processes of interest to dry sliding were introduced, and the irreversible entropy generated by these processes were quantitatively presented, see section 5.4. In consideration of equations (22), (17) and (18), the expressions for entropy generation presented in section 5.4 for the dissipative processes operative at a sliding interface, and *common to both friction and wear*, could result in *unified* friction and wear models.

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