

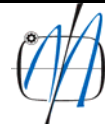


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ENTROPY AND DISSIPATIVE PROCESSES OF FRICTION AND WEAR

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Abstract: Friction and wear, often treated as unrelated, distinct phenomena, are manifestations of the same dissipative physical processes occurring at sliding interfaces. Friction force dissipates power and generates entropy. Wear irreversibly changes a material structure, often with loss of material. Associated with both friction and wear is production of irreversible entropy by interfacial dissipative processes. This article relates friction and wear through the irreversible dissipative processes occurring at sliding interfaces and the concomitant entropy produced. First, friction, wear and laws of thermodynamics are reviewed. Dissipative processes common to sliding interfaces and associated with types of friction and wear are identified and discussed. Finally, friction and wear are related to these processes, and to each other, via the Degradation-Entropy Generation Theorem, which formulates wear in terms of the irreversible entropy produced, and a combination of the first and second laws of thermodynamics that relates work of friction to the irreversible entropy of the dissipative processes.

Keywords: Friction, Wear, Entropy, Degradation, Dissipative Processes

1. INTRODUCTION

Historically, friction and wear have been studied and treated [1], [2], [3] as separate, unrelated phenomena. In fact, friction and wear are intimately related, being different physical manifestations of the same physical processes that occur within tribological interfaces. These processes are dissipative and irreversible: a power loss and permanent restructuring of material occurs.

Methods for investigating friction and wear have generally been heuristic. In 1995 Ludema's literature [4] survey of friction and wear modelling noted a preponderance of friction and wear mechanisms, based on many different physical principles, expressed in terms of many different variables, with little in common. The scope and applicability of most models was limited primarily to the specific system examined.

Friction force resists motion. Static friction force is usually larger than kinetic friction force, but dissipates no power. Non-conservative kinetic friction always dissipates power, and consistent with the second law of thermodynamics, always generates irreversible entropy.

Wear is usually classified as a permanent loss of material, but also includes transfer and back transfer phenomena. Wear always involves a irreversible and permanent reordering of a material's structure. As such, fundamental principles associated with the second law of thermodynamics guarantees that irreversible entropy must be produced during any material transformation, including those associated with wear.

Losses from friction force provide all or at least some of the energy that drives the irreversible material changes associated with wear. Friction is necessary for sliding wear. As such, at least some of the irreversible entropy produced by friction and wear are the same, or at least related.

Manufacturing, which transforms nature's raw materials into highly organized finished components, reduces entropy. Aging or degradation from friction and wear tends to return these components back to natural states. Accordingly, entropy must monotonically increase to be consistent with laws of thermodynamics [5]. Applying this concept to wear, Doelling et al [6] experimentally correlated wear with "entropy flow" produced by accompanying irreversible processes

occurring at a wearing surface. Wear was roughly proportional to the entropy produced. Here sliding of copper on steel was steady and under boundary lubricated conditions. Entropy flow $dS_e = dQ/T$ was estimated by measuring heat flow dQ and contact temperature T via thermocouples embedded in the slider. Under steady sliding conditions, system entropy change $dS = 0$, and entropy flow approximately equalled the entropy generated by friction and wear, as suggested by equation (2). Additional experiments involving dry sliding of brass on stainless steel [7] with different geometry, produced similar results. Later, and Ling et al [8] reconsidered the irreversible entropy.

Recently Bryant et al [9] formulated and proved the “Degradation Entropy Generation Theorem,” (DEG theorem) which established a general relationship between rate of degradation of systems and the rate at which entropy is produced by underlying dissipative irreversible processes. The theorem identified a generalized “*degradation force*” in terms of its generalized “*thermodynamic force*” counterpart, and showed the rate of degradation to be a linear combination of the rates of entropy produced by each of the dissipative processes. Bryant et al [9] further showed that both Archard’s wear law [10] and fretting wear, which does not follow [11] the Archard law, are subsets of the DEG theorem.

This article formulates models for friction and wear, based on fundamental principles of thermodynamics, and understanding of dissipative interfacial processes. Thermodynamics and the dissipative processes common to tribological interfaces will be briefly reviewed. Then, models of friction and wear will be formulated based on the irreversible entropy produced by friction and wear. Since this irreversible entropy is common to both friction and wear, the models will be intimately related.

2. REVIEW OF THERMODYNAMICS AND DISSIPATIVE PROCESSES

2.1 Laws of thermodynamics

The first law of thermodynamics [5]

$$dE = dQ - dW + \sum \eta_k dN_k \quad (1)$$

balances change of internal energy E , heat flow Q , work W , and reaction energy posed via chemical potentials η_k and molar masses N_k . The second law of thermodynamics [5]

$$dS = dS' + dS_e \quad (2)$$

balances entropy change to production of irreversible entropy dS' and entropy flow dS_e . Entropy S is defined via $dS = dQ/T$. The second law demands $dS \geq 0$, with $dS = 0$ for systems at equilibrium or steady state. Entropy flow arises from heat dQ and matter $\sum \eta_k d_e N_k$ crossing a control volume, such that

$$TdS_e = dQ + \sum \eta_k d_e N_k \quad (3)$$

Change in molar mass of material

$$dN_k = dN_k' + d_e N_k \quad (4)$$

can occur through reaction dN_k' or mass flow $d_e N_k$. Combining equations (1) through (4) leads to

$$TdS' = TdS - dE - PdV - d\bar{W} + \sum \eta_k dN_k', \quad (5)$$

which relates changes in irreversible entropy S' to work \bar{W} not included in pressure-volume PdV , internal energy, system entropy, and reactions.

Attempts [12], [13], [14], [15], [16], [17] to apply laws of thermodynamics to tribological systems in a traditional and rigorous manner had limited success, due to extreme complexity of the resulting equations and concomitant difficulty of solution.

2.2 Dissipative processes of tribology interfaces

Friction and wear are related through common dissipative processes operative at sliding interfaces. Reference [18] reviewed friction and wear, with goal of identifying prevalent dissipative processes at tribological interfaces, and estimating the irreversible entropies produced. Dissipative processes in reference [18] included:

- Adhesion of surfaces and films, associated with adhesive wear and adhesive friction, with entropy change

$$\Delta S' = \frac{\gamma}{T_m} \Delta A_s,$$

where interface surface energy γ is the work per unit area to create new surface area ΔA_s and T_m is the local temperature of the media.

- Plastic deformation, associated with abrasive wear, friction ploughing, and/or cutting, with entropy change

$$\Delta S' = \frac{U_c}{T_m} \Delta V$$

- where U_c is work (plastic deformation or cutting) expended per unit volume ΔV affected, and T_m is temperature of the affected material media.

- Fracture, associated with fatigue wear and surface damage, with entropy change

$$dS' = \frac{G - 2\gamma_0}{T_{cr}} da,$$

where a is crack length, $G = -\partial U_s / \partial a$ is the energy release rate dependent on strain energy U_s , γ_0 is surface energy, and T_{cr} is temperature of the cracked material at the crack tip.

- Phase changes, associated with surface melting, and recrystallization of metals, with entropy change

$$\Delta S' = \frac{\Delta H}{T_{phase}},$$

where ΔH 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.

- Chemical reactions, associated with chemical and oxidation wear, with entropy change

$$dS' = \frac{\bar{A}}{T_m} d\xi, \quad \bar{A} = \sum_{\text{reactants}} \kappa_i \eta_i - \sum_{\text{products}} \kappa_i \eta_i$$

where chemical affinity \bar{A} depends on the chemical potentials η_i and stoichiometric coefficients κ_i of the reaction. Since the stoichiometry of the reaction relates changes of molar masses dN'_i of reactants and products, extent of reaction ξ has differential change $d\xi = \pm dN'_i / \kappa_i$ where minus pertains to reactions, and plus to products.

- Diffusion, associated with gradient induced migration of material, with entropy change similar to that for chemical reactions.
- Mixing, which for tribology involves mixing of third body [19], [20] material entrained between surfaces, with molar entropy change

$$\Delta S' = -R \sum_i^n \frac{N_i}{N} \ln \frac{N_i}{N}, \quad N = \sum_i^n N_i.$$

Here R is the universal gas constant, N_i denote molar masses of n species, and ratios N_i/N denote molar fractions.

- Heat transfer, associated with diffusion of heat dQ from region of higher temperature T_h to lower temperature T_l , with entropy change

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

For each of these dissipative processes, the entropy produced was a product of a weighting term and a differential or difference of a

phenomenological variable. Thus, each of the aforementioned entropies can be written in one of the two forms

$$dS' = X d\zeta \quad (6a)$$

$$\Delta S' = X \Delta \zeta \quad (6b)$$

where X is the weighting function and ζ is the phenomenological variable.

3. THERMODYNAMICS OF FRICTION AND WEAR

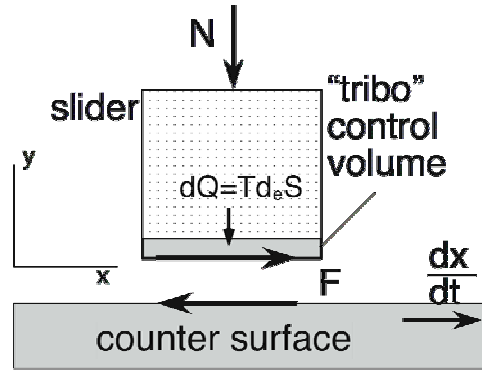


Figure 1. Slider and counter surface, with control volume enclosing interface of dissipative processes.

3.1 Assessment of Friction Force

Figure 1 depicts a slider on counter surface running at speed dx/dt , with normal and friction forces N and F . Heat $dQ = T d_e S$ is shed from friction dissipation. If equation (5) is applied to the tribological control volume of figure 1, the work term $d\bar{W} = Fdx + Ndy$, where dx and dy are differential displacements and N and F are normal and tangential forces at the contact interface along directions x and y . The term dS' on the left side of equation (5) will consist of a sum of entropy production terms, such as those discussed in section 2.2, and having the form of equations (6). Under simplifying conditions of steady state sliding, $dE = dS = 0$, and equation (5) becomes

$$\sum_j T_j X_j d\zeta_j = -Fdx - Ndy - PdV + \sum_k \eta_k dN'_k. \quad (7)$$

Differentials dx , dy , and dN'_k in equation (7) are linearly independent of each other. Displacements dx and dy , are orthogonal. Geometrically displacements are independent of molar concentrations dN'_k , which are either linearly independent of each other, or related via stiochiometry, see chemical reactions paragraph of section 2.2. Equation (7) suggests that for the dissipative processes on the left side to be related to the work performed by contact forces, the

differentials of the various phenomenological variables must be related to dx and dy , otherwise all terms multiplying differentials in equation (7) would vanish. Regrouping equation (7) yields

$$\begin{aligned} & \left(F + P \frac{dV}{dx} + \sum_j^{nx} T_j X_j \frac{d\zeta_j}{dx} \right) dx \\ & + \left(N + P \frac{dV}{dy} + \sum_j^{ny} T_j X_j \frac{d\zeta_j}{dy} \right) dy \\ & + \sum_j^n \left(T_j X_j \frac{d\zeta_j}{d\xi_j} - \eta_j \right) d\xi_j = 0 \end{aligned} \quad (8)$$

where the final term have molar masses dN'_k grouped together into $d\xi_j$ for convenience.

Linear independence of the differentials in equation (8) asserts that the expressions within the parentheses must vanish, rendering friction force and normal force as

$$F = -P \frac{dV}{dx} - \sum_j^{nx} T_j X_j \frac{d\zeta_j}{dx} \quad (9a)$$

$$N = -P \frac{dV}{dy} - \sum_j^{ny} T_j X_j \frac{d\zeta_j}{dy} \quad (9b)$$

The pressure term in equation (9a) will likely be small, since the kinetic friction of interest is dissipative, and hydrostatic pressure in solids has no influence on plastic deformation.

3.2 DEG Theorem and Assessment of Wear

The Degradation-Entropy Generation Theorem, relates degradation to the concomitant irreversible entropy produced. The theorem, formulated and proved in reference [9], realizes that degradation is rendered by dissipative processes characterized by energies $p_i = p_i(\zeta_1, \zeta_2, \dots, \zeta_m)$, $i = 1, 2, \dots, n_p$ that in turn depend on time dependent phenomenological variables $\zeta_i = \zeta_i(t)$, $j = 1, 2, \dots, m$. For degradation such as wear, $w = w\{p_i(\zeta_i)\}$. Since wear is irreversible, the second law demands the change be accompanied by production of irreversible entropy. Further, this entropy must exhibit a similar sequential dependence $S' = S'\{p_i(\zeta_i)\}$ on processes and variables. With this, the chain rule renders rates of degradation (wear) and entropy production

$$\frac{dw}{dt} = \sum_i \sum_j \left(\frac{\partial w}{\partial p_i} \frac{\partial p_i}{\partial \zeta_i^j} \right) \frac{\partial \zeta_i^j}{\partial t} = \sum_i \sum_j Y_i^j J_i^j \quad (10)$$

$$\frac{dS'}{dt} = \sum_i \sum_j \left(\frac{\partial S'}{\partial p_i} \frac{\partial p_i}{\partial \zeta_i^j} \right) \frac{\partial \zeta_i^j}{\partial t} = \sum_i \sum_j X_i^j J_i^j \quad (11)$$

where $X_i^j = \partial S' / \partial p_i (\partial p_i / \partial \zeta_i^j)$, $J_i^j = \partial \zeta_i^j / \partial t$, and $Y_i^j = \partial w / \partial p_i (\partial p_i / \partial \zeta_i^j)$. The DEG theorem, proved based on the structural similarities of equations (10) and (11), is only stated here.

DEG Theorem: Given an irreversible material degradation consisting of $i=1, 2, \dots, n$ dissipative processes, characterized by energies $p_i = p_i(\zeta_i)$, dependent on phenomenological variables $\zeta_i = \zeta_i(t)$, $j=1, 2, \dots, m_i$ that are time dependent. Assume the degradation can be described by a degradation measure, $w = w\{p_i(\zeta_i)\}$, non-negative and monotonic in the process energies p_i . Then with degradation rate per unit time $\dot{w} = dw/dt$, where “dot” refers to time d/dt , the following is true:

- The degradation rate $\dot{w} = \sum B_i \dot{S}_i$ is a *linear combination* of the components of entropy production $\dot{S}_i = \sum_j X_i^j J_i^j$ of the dissipative processes p_i , where X_i^j are generalized thermodynamic forces and J_i^j are generalized thermodynamic flows [5].
- Degradation components $\dot{w}_i = \sum_j Y_i^j J_i^j$ proceed at rates J_i^j determined by entropy production.
- The generalized “degradation forces” Y_i^j are *linear functions* $Y_i^j = B_i X_i^j$, where degradation coefficients $B_i = \partial w / \partial S' |_{p_i}$ are slopes $\partial w / \partial S'$ of the degradation versus entropy production curves, with process p_i active.

The DEG theorem has been applied to wear [9], [7], wherein the degradation measure w is volume lost during sliding, the phenomenological variable ζ is distance slid x , and the process energy p depends on sliding and environmental conditions.

4. EXAMPLE

For sliding of ductile metals, the dominant dissipative process p is plastic deformation [21] concentrated in a thin severely deformed region local to the sliding contact [22]. The amount of plastic work dissipated is dependent on distance slid x . Tsuya [22] measured friction force for copper sliding on steel and measured the intensity of plastic strain in the near surface layers, deemed the severely deformed region. Rigney and Hirth [21] compared the measured friction force to an estimate of the plastic work dissipated per unit volume, using the yield strength in shear and the plastic strains, and found that the friction force could be estimated as the plastic work per volume dissipated per distance slid. This is consistent with the second term of equation (9a).

Wear can be estimated by the DEG theorem. Here wear $w=w\{p(x)\}$ and irreversible entropy $S'=S'\{p(x)\}$. With surface layers enclosed by the "tribo control volume" in figure 1; steady speed and force rendering a stationary process with $dE = dS = 0$; small energy transport effects due to wear's usually tiny material loss, allowing the system to be treated as closed; no reactions; and all friction work dissipated within the wear control volume, the second law (2) gives $dS' = -dS_e$ and the first law (1) gives

$$dW = dQ = TdS_e = -TdS' \quad (12)$$

The rate of irreversible entropy via equation (11) is

$$\frac{dS'}{dt} = \frac{\partial S'}{\partial p} \frac{\partial p}{\partial x} \frac{dx}{dt} = \frac{F}{T} \frac{dx}{dt} \quad (13)$$

Contact temperature T arose via the outer equality of equation (12) coupled with $dp = -dW$, which equated the plastic work dissipated in the control volume to the work dW applied. Because $dS'/dt \geq 0$ and $T \geq 0$, F and dx/dt must have same signs, consistent with friction opposing sliding velocity. From the equalities following equation (11), $J = dx/dt$, $dp/dx = F$ and $X = \partial S'/\partial p$ ($\partial p/\partial x = F/T$). The degradation coefficient defined in the DEG theorem becomes

$$B = \frac{Y}{X} = \left. \frac{dw}{dS'} \right|_p \quad (14)$$

Applying eqs. (10) and (13) yields

$$\frac{dw}{dt} = YJ = BXJ = B \frac{dS'}{dt} = \frac{BF}{T} \frac{dx}{dt} \quad (15)$$

References [6], [7], [9] compared equation (15) to Archard's wear law $\frac{dw}{dt} = \frac{k}{H} N \frac{dx}{dt}$ expressed with time derivatives, to relate wear coefficient $k = B \frac{\mu H}{T}$ to the degradation coefficient B . Here H is hardness and μ is friction coefficient. With B extracted from measured wear versus entropy flow curves similar to figure 2 via equation (14), the

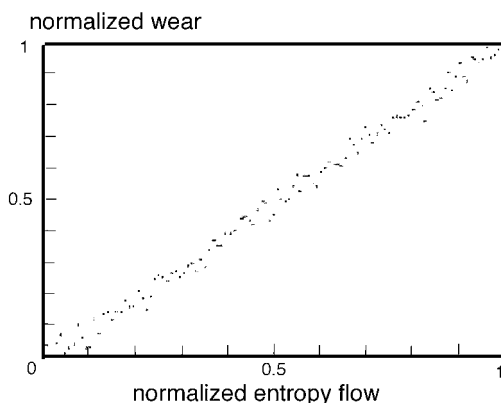


Figure 2. Normalized wear vs. normalized entropy flow, extracted from reference [7].

wear coefficient so obtained compared within 5% of published wear coefficients [3] measured under same conditions. In figure 2, the abscissas and ordinates were normalized by the largest value measured. As mentioned in Introduction section 1, these methods were repeated and gave similar results for copper pin on steel drum under boundary lubrication [6], and brass ring on stainless steel ring under dry condition [7].

Of particular interest, to obtain his estimate of wear coefficient k , Rabinowicz [3] measured weight loss, normal force and distance slid. To get values of B in equation (14) via the data in figure 2, measured in references [6] and [7] were weight loss force, and temperatures, physical states fundamentally from [3].

5. SUMMARY, DISCUSSION AND CONCLUSIONS

Friction and wear were related through the common dissipative processes operative at a sliding interface. Processes prevalent at sliding interfaces and the entropy produced were identified. Through the DEG theorem and equations (9), wear and friction force were estimated.

The friction force and wear models presented here are consistent with concepts of Suh [1], which expresses total wear and total friction force as sums over components from different mechanisms. The sums over the dissipative processes in equations (9) and (10) are consistent with Suh's [1] concept, wherein the friction or wear mechanism is associated with one of more specific dissipative processes.

With these methods, friction and wear can be estimated, via a structured approach founded on laws of thermodynamics. Multiple mechanisms operating simultaneously can be formulated through equations (9) and (10). Here the entropies of the dissipative processes, acting as influence functions, provide the influence of specific dissipative processes on the total friction and wear. The mechanics of the friction-wear mechanism can then be embedded in energy-entropy expressions of the dissipative processes. Equations (9) and (10) can sift out the friction and wear manifestations of the dissipative processes.

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