



# Article Evaluating Degradation Coefficients from Existing System Models

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**Abstract:** A generalization of the Degradation-Entropy Generation (DEG) theorem to multi-disciplinary multi-physics system-process analysis via a combination with pre-existing system models is presented in this article. Existing models and the DEG methodology are reviewed, and a method for evaluating degradation coefficients  $B_i$  is proposed. These coefficients characterize the system's transformation based on active dissipative mechanisms, including temperature effects. The consistency of entropy generation in characterizing degradation is then inherited by these often-empirical system models, thereby rendering them more robust and applicable to similar systems without the need for numerous tests and measurements for model corrections. The approach applies to all systems and can quickly analyze and predict a system's performance and degradation, even in the absence of experimental data (using known properties and material constants). Demonstrated applications herein include mechanically loaded systems (frictional wear, grease shearing, fatigue loading), electrochemical energy systems, thermal processes, and others.

**Keywords:** system analysis; degradation; thermodynamics; entropy generation; fatigue; lubricating grease; electrochemical systems; batteries; frictional wear

# 1. Introduction

System characterization models are discipline specific. Formulations are often derived from the natural laws governing the prevalent active interactions using properties that characterize the system and the process. For example, a strain-loaded system is often characterized using the system's strength (or stress  $\sigma$ ) and the strain process rate (or strain rate  $\varepsilon$ ); electrochemical systems are characterized using the system's electrochemical potential (or voltage *E*) and the discharge/charge process rate (or current *q*); tribological systems use friction force *F* (the product of the system's friction coefficient and normal force, often the system's weight) and interfacial velocity *x*; thermal processes use the system's heat capacity *C* (the product of its mass and specific heat capacity) or thermal conductivity *k*, and the temperature change rate *T* or gradient  $\nabla T$  (also the heat transfer rate); and mass transfer processes use the system's pressure *P*, density  $\rho$  (or specific volume *v*) or concentration and mass flow rate *m*. Note that in the above examples, interactions are appropriately described by conjugating system variables with process variables.

Engineers in industry combine time-invariant system response simulations with experimental data to characterize a system. In fields where established simulation tools are not available, statistical analyses and curve fits of measured data are used. A large number of system- and process-specific empirical models are published regularly, which are not applicable to other similar systems when parameters change. Individual manufacturers and laboratories utilize vast research and development resources in characterizing a system, thereby reducing resources available for optimizing or improving the system. In this study,



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). existing multi-physics system models are reviewed and combined with the Degradation-Entropy Generation DEG theorem [1]. Degradation coefficients are obtained to unify all system analyses consistently via one approach, irrespective of the base model, response parameter or material constant selected for analysis.

#### Entropy Generation, a Measure of System Degradation

The consistency of entropy generation in characterizing irreversibilities in systems and processes continues to attract degradation/failure experimentalists from various fields. Recent multi-disciplinary works have shown excellent correlations between entropy-based failure models and experimental measurements [2]. Basaran et al. [3–7] defined damage, via Boltzmann's entropy, as a measure of the change in order/disorder. Using several experimental verifications including solder joints and composites, the authors demonstrated high model-to-experiment correlation. This series of works led to the formulation of the unified mechanics theory [8] which combines a thermodynamic state index with otherwise steady-state physical laws to render them more consistent with experimental observations. Combining thermodynamic laws with damage mechanics, Sosnosvskiy and Sherbakov [9,10] introduced the tribo-fatigue entropy to measure local damage accumulation in a mechanical system. Their approach, termed mechanothermodynamics, includes damage distribution in a volume, correlating well with measurements. Entropy-based works of Khonsari et al. [11–20] have shown consistently accurate characterizations of various mechanical systems under diverse forms of loading, such as grease shearing, metal and composite laminate fatigue as well as interfacial sliding wear. Cuadras et al. [21–23] used entropy generation to estimate damage in resistors, capacitors and batteries, showing consistent correlations between model and measurements. Various works by Bryant et al. [1,24–26] characterizing frictional wear via entropy transfer out of a tribo-control volume led to the formulation of the universally consistent Degradation-Entropy Generation (DEG) theorem [1], which has been shown highly accurate in characterizing real systems undergoing spontaneous degradation often leading to failure. Using several experimental verifications, Osara and Bryant [2,27-30] extended the original DEG theorem to unsteady interactions and nonlinear degradation of multi-component multi-physics system-process interactions including batteries, grease and general fatigue. This article presents a simple, direct and practical approach for evaluating system-characteristic degradation coefficients via a combination of existing system models (theoretical, semi-empirical or empirical) with the minimum entropy generation. The approach is demonstrated for multidisciplinary systems. To keep the discussion herein concise and focused on the primary objective, detailed thermodynamics derivations and discussions are excluded from this article. In the Appendix A, a short summary of relevant foundational irreversible thermodynamics concepts is presented, with several references provided for further reading.

#### 2. Existing System Characterization Models and Material Constants

Here we briefly review a few models selected from the literature for diverse engineering systems.

#### 2.1. Grease

The rheological properties—thixotropy and viscoelastoplasticity—of grease, a semisolid, make it only partially compliant with Newtonian physics. Manufacturers use inhouse application-dependent half-empirical grease models curve-fitted from hundreds of data sets. NLGI classifications of grease types are given in ranges [31] to provide manufacturers a margin for experimental inconsistencies. Over time, extensive grease research has led to several models describing grease behavior under load. Most of these models are based on very slow shearing of grease at constant temperature, to minimize plastic deformation and strength dissipation, which in turn yields the most consistent experimental correlations. Validity of grease models is often limited to certain operating conditions. Shear stress  $\tau$ , shear strain rate  $\dot{\gamma}$  (also shear rate or strain rate), viscosity  $\eta$ , penetration, thixotropic index and shear modulus *G* are some commonly used grease characterization parameters and material constants. Table 1 highlights a few grease characterization models for various operational mechanisms.

Table 1. Highlights of a few commonly used grease models.

Operational Mechanism	Transformation Measure	System Model	Notes
		Power-law: $\tau = K\dot{\gamma}^n$	Earliest widely adopted model, limited to a narrow range of medium shear rates [32]. <i>K</i> is consistency factor and <i>n</i> is flow index.
		Herschel-Bulkley: $\tau = \tau_y + K \dot{\gamma}^n$	Currently the most widely used. Good correlation with data at shear rates between 0.001 and 1000 s <sup>-1</sup> [33,34]. $n \approx 0.5$ for greases.
	Shear stress (Yield stress $\tau_y$ )	Sisko [35]: $\tau = K\dot{\gamma}^n + \eta_b\dot{\gamma}$	Typically applied to high shear rates (>1000 s <sup><math>-1</math></sup> ).
Mechanical	, <i>y</i> ,	Maxwell: $\frac{d\tau}{dt} = G\left(\dot{\gamma} - \frac{\tau}{\eta}\right)$	Widely used to describe viscoelasticity using a spring in series with a viscous damper. Gives an accurate time-based shear stress response at constant shear but does not accurately describe response to constant shear stress [36].
		Gecim and Winer [37]: $\dot{\gamma} =$ $\frac{1}{G_{\infty}} \frac{d\tau}{dt} + \frac{\tau_L}{\mu} tanh^{-1} \left(\frac{\tau}{\tau_L}\right)$	Adds a nonlinearity to the Newtonian component in the Maxwell model using the limiting shear stress $\tau_L$ concept [37].
	Shear strain	Kevin-Voigt: $\frac{d\gamma}{dt} = \frac{\tau - \gamma G}{\eta}$	Connects the spring and damper in parallel and accounts for the constant shear stress time-dependent strain response. Does not accurately predict relaxation [36].
		Mewis [38]: $\frac{d\eta}{dt} = k [\eta_e(\dot{\gamma}_1) - \eta]^n$	Gives rate of change of viscosity at constant shear rate. Constants $k_i$ are empirically determined.
	Viscosity	$Cross [39]:$ $\frac{dN}{dt} =$ $k_2 P - (k_0 + k_1 \dot{\gamma}_1^m) N$	Gives the rate of bond breakdown in grease in terms of number of linkages <i>N</i> . The number of links per chain <i>N</i> is further related to viscosity.
	Shear stress	$\tau = \gamma_0 G \Big[ exp\Big(\frac{E_a}{RT}\Big) \Big]$	Uses the Arrhenius formulation to describe grease response to temperature changes [36]. $E_a$ is activation energy, $R$ is universal gas constant.
Thermal	Yield stress	Lugt [32]: $\frac{\tau_y}{\tau_{y0}} = exp\left[\left(\frac{T_0 - T}{b}\right)ln2\right]$	Extends the Arrhenius formulation to yield stress $\tau_y$ . Constant <i>b</i> is empirical.
	Viscosity	Lugt [32]: $\eta = \eta_0 \left[ exp\left(\frac{E_a}{RT}\right) \right]$	Arrhenius formulation using viscosity.
	Shear stress	Osara [2]: $\frac{d\tau}{dt} = \tau_0 kexp(-kt)$	Based on Rhee's [40] % degradation = $e^{-kt}$
Chemical	Viscosity	Osara [2]: $\frac{d\eta}{dt} = \eta_0 kexp(-kt)$	Extends Rhee's [40] % degradation = $e^{-kt}$
	Mass	Lugt [41]: $\frac{dm}{dt} = m_0 kexp(-kt)$	to viscosity. Describes oxidation in grease via mass change. Here, <i>k</i> is rate constant.

In Table 1, the mechanical grease shearing models combine Newtonian, Hookean and power law formulations—the thermal and chemical models are Arrhenian—with experimental measurements. These models are limited to a range of shear rates, grease types and load types, and deviate significantly when applied to uncontrolled grease degradation. Manufacturers apply Table 1 models, and others, with empirical corrections from measured data.

# 2.2. Electrochemical Energy Storage

Energy storage systems such as batteries and capacitors provide portable storage of electrochemical energy. Rechargeable energy storage systems continue to gain significance

in consumer devices and industrial facilities. Safety and durability issues have plagued the battery industry since the first battery was made, limiting the availability of a battery's energy during operation. Typical battery life is the number of full discharge-charge cycles before available charge content drops below 80% of initial charge capacity. Battery instability is exacerbated by fast and/or deep cycling. The complex internal kinetics of batteries limit the validity of available characterization models to battery types, configurations and scales. Battery materials researchers and manufacturers rely on voltage-charge curves and Coulomb-counted charge transfer obtained from controlled low-rate cycling, for performance analysis. These are inconsistent when the battery undergoes typical in-operation use—irregular and abusive. Battery models, often empirical, use voltage and charge as characterization parameters. Physics-based models use electrochemical energy. Table 2 reviews a few electrochemical system models or "figures of merit" [42] in the literature. Here, *E* is voltage, *R* is resistance, *q* is charge rate or current, *q* is charge content, *F* is Faraday's constant and *t* is time.

Transformation Measure	System Model	Notes
Voltage	$E = R\dot{q}$	Ohm's law: voltage as a function of current and resistance.
Charge content	$q = q_0 \pm \int_{t_0}^t \dot{q} dt$	Charge levels via Coulomb counting.
Concentration change	$\Delta c = \frac{\varphi \dot{q} t}{nFE}$	Evaluates active species concentration change via Faraday's electrolysis laws, where $\varphi$ is current efficiency, <i>t</i> is time, <i>n</i> is number of active species and <i>F</i> is Faraday's constant.
Internal resistance	$Z = \frac{E_{OC} - E}{\dot{q}}$	A measure of the battery's degradation via its resistance to charge flow, where $E_{OC}$ is open-circuit voltage.
Fractional conversion	$X_A = \frac{m_0 \pm m}{m_0}$	Fraction of active species converted during electrochemical reaction, where <i>m</i> is amount of reactant (mass or number of moles).
Mass transport coefficient	$k_L = \frac{\dot{q}_L}{AnFc}$	Measures flow/consumption of active species in electrochemical systems with significant mass transfer/diffusion, where $\dot{q}_L$ is limiting current, $A$ is electrode area and $c$ is active species concentration.

 Table 2. A review of a few selected electrochemical system models [42].

# 2.3. General Fatigue

All dynamically loaded non-fluid systems eventually fail. Solids are analyzed using combinations of Newtonian and Hookean mechanics. For metals, which show significant elastic response to certain load magnitudes, steady-state three-dimensional Hookean-based simulations are combined with experimental load-to-failure tests to establish structural integrity under fatigue loading. To avoid unexpected failure due to the inconsistencies in characterization approaches and in situ material response, safety factors are applied during design stages. For high-cycle fatigue (HCF), stress-based approaches such as the stress-life and Modified Goodman curves are used. Components prone to low-cycle fatigue (LCF) are designed using a combination of strain-based models such as Coffin-Manson's strain-reversals relation [43] and Morrow's plastic strain energy density [44] with significant safety margins. Table 3 lists a few commonly used fatigue measures ( $\sigma$  = stress or strength, M = moment,  $M_t$  = torque, I = second moment of inertia, J = polar moment of inertia,  $\sigma'_f$  = fatigue strength coefficient,  $\varepsilon'_f$  = fatigue ductility coefficient, N = number of cycles).

Transformation Measure	System Model	Notes
Stress/Strength	Bending Stress: $\sigma = \frac{My}{T}$ Shear Stress: $\tau = \frac{M_t y}{J}$ Fatigue Strength (HCF): $\sigma_N = \frac{\sigma'_f^2 (4E6)^b N^b}{\sigma_e}$ $\sigma_N = \sigma_0 \left(\frac{1+N/N_e}{N}\right)^{\alpha}$	Based on Hookean mechanics, which assumes elastic response to loading. The fatigue strength ( $\sigma_N$ ) equations are obtained from load-to-failure tests on standard specimens. Special factors are included to account for materials, surface finishes and other physical aspects of the specimen. Typically used in high-cycle fatigue analysis. Here, <i>y</i> is distance, $\sigma_e$ is endurance strength, $N_e$ is endurance cycle number, and <i>b</i> and $\alpha$ are empirically determined parameters.
Strain	$\varepsilon_a = \frac{\sigma'_f}{E} \left( 2N_f \right)^b + \varepsilon'_f \left( 2N_f \right)^c$	Coffin-Manson equation: empirically determined plastic strain response to loading, in addition to elastic strain. Typically used for low-cycle fatigue, where $b$ and $c$ are evaluated from empirical load-to-failure data. $N_f$ is number of cycles to failure.
CDM Damage	$D = \frac{-D_{N_f-1}}{lnN_f} ln \left[ 1 - \frac{N}{N_f} \right]$	Based on Continuum Damage Mechanics, the damage variable <i>D</i> predicts a logarithmic load-to-failure response [45].
Fracture rate	$\frac{da}{dN} = C(\Delta K_1)^m$	Paris law for predicting crack growth, where <i>a</i> is crack length, $\Delta K_1$ is stress intensity range per cycle, <i>C</i> and <i>m</i> are empirical material constants.

**Table 3.** A few commonly used fatigue models [43,45].

Fatigue models in Table 3 are either steady-state physics-based or load-to-failure empirical [43]. Their correlations with actual in-operation data are inconsistent, requiring significant corrections and safety factors. Highly conservative design (or over-designing), which wastes resources, is often an undesired result of using these approaches.

# 3. The Degradation-Entropy Generation (DEG) Theorem

Bryant et al. [1], following a series of experimental studies of friction wear, proposed the Degradation-Entropy Generation DEG theorem which linearly correlates a degradation measure w and entropy generation  $S'_i$ . Mathematically,

$$\dot{w} = \sum_{i} B_{i} \dot{S}'_{i} \tag{1}$$

where degradation/transformation coefficients  $B_i = \frac{\partial w}{\partial S'_i}\Big|_{p_i}$  are obtained as slopes of degradation measure w, with respect to entropy generations  $S'_i$ ; the  $\Big|_{p_i}$  notation indicates active processes  $p_i$  numbered by index *i*. Details of the DEG theorem, including statements and proof, can be found in [1]. Frictional wear [1,24–26] and fatigue [11–17] experiments verified the theorem. A breakdown of entropy generation can be found in this article's Appendix A. Osara and Bryant [2,27–30], via a combination of Equations (A3) and (A4) (see Appendix A) with Equation (1), instantaneously characterized unsteadily loaded multicomponent multi-physics systems, with verification using measured data from grease aging, lithium-ion battery and lead-acid battery degradation, and general fatigue experiments.

#### 3.1. DEG Methodology Procedure

Bryant et al. proposed a structured approach for applying the DEG theorem to degradation analysis: identify and measure the degradation measure w and active process energies  $p_i$  (or powers); evaluate entropy generation  $S'_i = S'_i(p_i)$  caused by the  $p_i$ ; relate degradation measure to entropy generation terms to obtain transformation coefficients. When measurements are available, the extended approach for instantaneous analysis by Osara and Bryant, presented in recent publications [2,27–30], is recommended. With entropy defined as the quotient of energy and temperature, the DEG approach subsumes temperature effects.

#### 3.2. DEG Coefficients

DEG coefficients  $B_i$  show the system's natural response to active dissipative processes and conditions by estimating the processes' contributions towards system degradation and eventual failure. For monotonically aging systems, e.g., a solid under low-cycle fatigue loading, DEG coefficients from the first few time steps predict the system's normal operating path, and can be used for instantaneous health monitoring and failure detection. In non-reactive systems, load-to-failure DEG coefficients from a representative sample of the system can characterize other systems of the same composition undergoing similar processes in operation. In secondary (rechargeable) energy systems, DEG coefficients obtained from the first few cycles predict subsequent cycles to failure. Evaluating the  $B_i$  from Equation (1) indicates a high entropy generation rate yields a low  $B_i$  for a given transformation rate. Hence a high  $B_i$  (for primary interactions) is favorable to system transformation. This article combines the DEG theorem with existing system-specific models to obtain characteristic DEG coefficients.

#### 4. A Brief Review of Existing DEG Models

The DEG theorem is general and about the dynamics of loss and dissipation. The theorem renders the differential equations governing any loss or dissipative process, including material degradation and processes that dissipate energy, such as battery discharge and flow disruption. Several experimental studies have applied the DEG theorem to multiphysics systems undergoing steady, unsteady and abusive loadings with results yielding characteristic DEG coefficients.

## 4.1. Frictional Wear

Characterization of material wear occurring at a dynamic tribological interface is one of the earliest applications of the DEG theorem [1,24–26]. Relating measured wear volume to entropy transfer out of the interface (obtained from temperature-only measurements)

$$w_v = B_W \frac{Q}{T} \tag{2}$$

Bryant et al. obtained the wear-characteristic DEG coefficient. Here, *Q* is heat transfer into/out of the tribo-control volume.

#### 4.2. Grease

Osara and Bryant, applying the DEG theorem to grease degradation, obtained the shear stress-based relationship [27]

$$\int_{t_0}^t \tau dt = B_{\mu T} \int_{t_0}^t -\left(\rho c lnT + \frac{\alpha}{\kappa_T}\gamma\right) \frac{T}{T} dt + B_W \int_{t_0}^t -\frac{\tau \dot{\gamma}}{T} dt$$
(3)

Data from mechanical shearing of two grease types yielded DEG coefficients  $B_{\mu T} = -0.504$  Pa-s K/J and  $B_W = -10.36$  Pa-s K/J (NLGI 4 grease), and  $B_{\mu T} = -0.031$  Pa-s K/J and  $B_W = -10.38$  Pa-s K/J (NLGI 2 grease), obtained using strain rate-controlled grease shearing. In Equation (3),  $\rho$  is density, *c* is specific heat capacity,  $\alpha$  is thermal expansion coefficient,  $\kappa_T$  is isothermal shearability (the inverse of the shear modulus *G*) and other variables are as defined previously.

#### 4.3. Electrochemical Energy Storage Systems

Measurements from abusive cycling of several 6 V lead-acid and 3.7 V lithium-ion batteries verified the DEG battery model given as [28,30]

$$q = \int_{t_0}^t \dot{q} dt = B_{VT} \int_{t_0}^t \frac{qE}{T} dt + B_W \int_{t_0}^t \frac{E\dot{q}}{T} dt$$
(4)

where variables are as defined previously. Degradation coefficients obtained from battery discharge data are  $B_{VT}$  = 13.8 Ah K/Wh and  $B_W$  = 51.9 Ah K/Wh for lead-acid batteries; and  $B_{VT}$  = 113 Ah K/Wh and  $B_W$  = 76.6 Ah K/Wh for lithium-ion batteries.

#### 4.4. General Fatigue

Application of the DEG methods to fatigue yielded the strain-based model (for stresscontrolled loading) [29]

$$\varepsilon = \int_{t_0}^t \dot{\varepsilon} dt = B_{\mu T} S_{\mu T} + B_W S_W \tag{5}$$

where microstructurothermal (MST) entropy  $S_{\mu T} = -\int_{t_0}^t \left(\rho c lnT + \frac{\epsilon \alpha}{\kappa_T}\right) \frac{\dot{T}}{T} dt$  and load entropy  $S_W = -\int_{t_0}^t N_{dt} \frac{\sigma_N}{T} : \left[\dot{\epsilon}_{eN} + \left(\frac{1-n'}{1+n'}\right)\dot{\epsilon}_{pN}\right] dt$ . For very high-cycle fatigue and infinite life, assuming elastic (and isothermal) load, Equation (5) reduces to

$$\varepsilon = B_W \frac{\sigma_N}{T} \varepsilon_e. \tag{6}$$

For strain-controlled loading, stress response may be used as transformation measure. Data measured during low-cycle fatigue of a stainless-steel specimen SS 304 yielded DEG coefficients  $B_{\mu T} = 0.22$  (bending) and 0.42 (torsion); and  $B_W = -0.92$  (bending) and -1.96 (torsion).

# 4.5. Combined Adhesive and Abrasive Wear

Lijesh and Khonsari [19] presented a DEG model characterizing multiple wear modes. Combining frictional entropy generation—from frictional force F and velocity  $\dot{x}$ —with measured volumetric wear rate

$$w_{v} = B_{1} \int_{t_{0}}^{t_{1}} \frac{F_{1}\dot{x}_{1}}{T_{1}} + B_{2} \int_{t_{1}}^{t_{2}} \frac{F_{2}\dot{x}_{2}}{T_{2}} + B_{3} \int_{t_{2}}^{t_{3}} \frac{F_{3}\dot{x}_{3}}{T_{3}}$$
(7)

the authors obtained degradation coefficients from data measured on a tribometer with a stationary pin on a rotating disk:  $B_1 = 0.422 \text{ mm}^3 \text{ K/J}$  (for adhesion wear mode),  $B_2 = 0.436 \text{ mm}^3 \text{ K/J}$  (for transition wear, an unsteady process) and  $B_3 = 0.464 \text{ mm}^3 \text{ K/J}$  (for abrasion wear) for the three wear regions identified.

# 5. Degradation Coefficients from a Combination of the DEG Models and Other Existing Multi-Physics Models

To use the system-specific models in Section 2 (Tables 1–3), researchers and industry engineers have to adhere to strict assumptions, use specialized equipment and test several samples of the component or system. Since all systems dissipate energy which generates entropy during loading, a combination of the DEG theorem with an established system-specific governing equation can yield degradation coefficients that consistently characterize the systems. Simple or in situ measurements can then be used to evaluate entropy generated by the active processes. A concise discussion of entropy generation is presented in the Appendix A. Table A1 lists minimum (or pseudo-steady) entropy generation equations for various system-process interactions. In the absence of measurement capabilities, existing data in the literature can also be used to estimate values for a system's degradation coefficients.

For solid interfacial wear due to sliding friction governed by Coulomb's friction law  $F = \eta N$  and Archard's wear law  $\dot{w} = kN\dot{x}/H$ , minimum entropy generation rate, from Equation (A1) with X = F and  $\dot{J} = \dot{x}$ , is  $SI_{min} = \eta N\dot{x}/T$ . Via the DEG theorem, Equation (1), wear rate  $\dot{w} = B\eta N\dot{x}/T$  which, via comparison with Archard's wear law, yields degradation coefficient  $B = kT/\eta H$ . Here, *k* is wear constant, *T* is temperature,  $\mu$ is friction coefficient, *H* is the hardness of the softer material and  $\dot{x}$  is interfacial sliding velocity. Doelling et al., using an experimentally measured *B*, obtained a value of Archard's wear constant *k* similar to that obtained by Rabinowicz. This procedure can be applied to all and sundry systems, as demonstrated in the subsequent sub-sections for the previously reviewed systems.

## 5.1. Grease

Steady entropy generation rate due to mechanical shearing of grease, Table A1, is  $S_{I_{min}} = V\tau\dot{\gamma}/T$  and for chemical degradation,  $S_{I_{min}} = \frac{\mu m}{M_M T}$ . Thermal entropy rate due to temperature change, a transient phenomenon, is S = CT/T. V is volume,  $\tau$  is shear stress,  $\dot{\gamma}$  is shear strain rate, T is temperature,  $\mu$  is chemical potential,  $\dot{m}$  is mass flow rate,  $M_M$  is molecular mass and *C* is heat capacity. Presented in Table 4 are combinations of various system models (column 3) with DEG models (column 4) to yield degradation coefficients (column 5), as done for interfacial wear in the previous paragraph. In Table 4, Pen = penetration depth; see definitions of other variables in Table 1.

Mechanism	Measure	System Model	DEG Model	Degradation Coefficient
	Shear stress	$\begin{array}{l} \text{Maxwell:} \\ \frac{d\tau}{dt} = G\left(\dot{\gamma} - \frac{\tau}{\eta}\right) \end{array}$	$\frac{d\tau}{dt} = B \frac{V \tau \dot{\gamma}}{T}$	$B = \frac{TG}{V\tau\dot{\gamma}} \left(\dot{\gamma} - \frac{\tau}{\eta}\right)$
Mechanical	Shear strain	Kevin-Voigt: $\frac{d\gamma}{dt} = \frac{\tau - \gamma G}{n}$	$\frac{d\gamma}{dt} = B \frac{V\tau\dot{\gamma}}{T}$	$B = rac{T}{V au\dot\gamma\eta}( au-\gamma G)$
	Viscosity	Mewis: $\frac{d\eta}{dt} = k [\eta_e(\dot{\gamma}_1) - \eta]^n$ Cross: $\frac{dN}{dt} = k_2 P - (k_0 + k_1 \dot{\gamma}_1^m) N$	$\frac{d\eta}{dt} = B \frac{V \tau \dot{\gamma}}{T}$	$B = \frac{kT[\eta_e - \eta]^n}{V\tau\dot{\gamma}}$ $B = \frac{T[k_2P - (k_0 + k_1\dot{\gamma}^m)N]}{V\tau\dot{\gamma}}$
	Yield stress	H-B: $\tau = \tau_y + K\dot{\gamma}^n$ $\tau_y = 3E10 * Pen^{-3.17}$	$\tau = B \frac{V \dot{\gamma} \int_{t_N} \tau dt}{T}$	$B = \frac{T(\tau_y + K\dot{\gamma}^n)}{V\dot{\gamma}\int_{t_N} \tau dt}$
	Consistency	$Pen = (32.5 * 10^{31.7} \tau_y^{-0.315})$	$Pen = B \frac{V \dot{\gamma} \int_{t_N} \tau dt}{T}$	$B = \frac{T(32.5 \times 10^{31.7} \tau_y^{-0.315})}{V \dot{\gamma} \int_{t_N} \tau dt}$
	Thixotropic Index	$TI=rac{\eta_s}{\eta_{10s}}=rac{10( au-\gamma G)_s}{( au-\gamma G)_{10s}}$	$TI = B \frac{V \dot{\gamma} \int_{t_N} \tau dt}{T}$	$B = \frac{10T\tau_{\rm s}}{\dot{\gamma}_{\rm V}\tau_{\rm 10s}\int_{t_{\rm N}}\tau}$
Thermal	Yield stress	$rac{ au_y}{ au_{y0}} = exp\Big[\Big(rac{T_0-T}{b}\Big)ln2\Big]$	$ au_y = BClnigg[rac{T}{T_0}igg]$	$B_T = \frac{\tau_{y0} exp\left[\frac{T_0 - T}{b}ln2\right]}{Cln[T/T_0]}$
	Viscosity	$\eta = \eta_0 \Big[ exp \Big( rac{E_a}{RT} \Big) \Big]$	$\eta = BCln\left[rac{T}{T_0} ight]$	$B_T = \frac{\eta_0 \left[ exp\left(\frac{E_0}{RT}\right) \right]}{Cln[T/T_0]}$
	Shear stress	$\frac{d\tau}{dt} = \tau_0 kexp(-kt)$	$\frac{d au}{dt} = B \frac{\mu \dot{m}}{M_M T}$	$B_m = \frac{\tau_0 k M_M Texp(-kt)}{um}$
Chemical	Viscosity	$\frac{d\eta}{dt} = \eta_0 kexp(-kt)$	$\frac{d\eta}{dt} = B \frac{\mu \dot{m}}{M_M T}$	$B_m = \frac{\eta_0 k M_M Texp(-kt)}{\mu m}$
	Mass	$\frac{dm}{dt} = m_0 kexp(-kt)$	$\frac{dm}{dt} = B \frac{\mu \dot{m}}{M_M T}$	$B_m = rac{m_0 k M_M Texp(-kt)}{\mu m}$

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Table 4. Degradation	CUEINCIEINS HUI		Elease mou	C19	IEVIEWEU	111	Table 1.

# 5.2. Electrochemical Energy Storage Systems

For a battery or other electrochemical energy device governed by Ohm's law  $E = R\dot{q}$ , minimum entropy generation rate is  $S'_{min} = E\dot{q}t/T$ . Thermal entropy rate due to temperature change only is  $\dot{S} = C\dot{T}/T$ . Table 5 presents previously reviewed battery models (in column 2) which are directly compared (equated) to DEG models (in column 3) to yield degradation coefficients (column 4).

Measure	System Model	DEG Model	Degradation Coefficient
Voltage	$E = R\dot{q}$	$\frac{dE}{dt} = B \frac{E\dot{q}}{T}$	$B = \frac{T}{q}$
Charge content	$q = \int_{t_0}^t \dot{q} dt$	$q \stackrel{\text{dif}}{=} B \int_{t_0}^t \frac{Eq}{T} dt$ $\Delta c = B \frac{Eqt}{T}$	$B = \frac{\dot{T}}{E}$
Concentration change	$\Delta c = \frac{\varphi \dot{q} t}{nFE}$ $Z = \frac{E_{OC} - E}{\dot{q}}$	$\Delta c = B \frac{E\dot{q}t}{T}$	$B = \frac{T\varphi}{nFE^2}$ $B = \frac{T(E_{OC} - E)}{2}$
Internal resistance	$Z = \frac{E_{OC} - E}{q}$	$Z = B \frac{Eq}{T}$	$B = \frac{T(E_{OC} - E)}{E\dot{a}^2}$
Fractional conversion	$X_A = \frac{m_0 \pm m}{m_0}$	$X_A = B \frac{E\dot{q}}{T}$	$B = \frac{T(m_0 \pm m)}{Eqm_0}$
Mass transport coefficient	$k_L = rac{\dot{q}_L}{AnFc}$	$k_L = B rac{E \dot{q}}{T}$	$B = \frac{\dot{T}\dot{q}_L}{E\dot{q}AnFc}$

Table 5. Degradation coefficients from existing electrochemical energy storage models reviewed in Table 2.

#### 5.3. General Fatigue

Similar to grease, a semi-solid, mechanically loaded solid materials, via stress  $\sigma$  and cyclic strain amplitude  $\dot{\epsilon}$ , generate steady-state entropy at rate  $\dot{S}I_{min} = \sigma : \dot{\epsilon}/T$  and for chemical degradation including metal rust,  $\dot{S}I_{min} = \frac{\mu m}{M_M T}$ . Thermal entropy rate due to temperature change is  $\dot{S} = CT/T$ . In the absence of measured stress and strain, empirical relations can be used to estimate entropy generation. For steels, combining elastic energy  $W_e$  with Morrow's cyclic plastic strain energy  $W_p$  gives  $\dot{S}I_{min} = \dot{W}/T = (\dot{W}_e + \dot{W}_p)/T = \frac{\sigma_N}{T} : [\epsilon_{eN} + \epsilon_{pN}(\frac{1-m'}{1+n'})]$ , where the subscript N denotes cyclic. In Table 6, previously reviewed fatigue models (column 2) are combined with DEG models (column 3) to obtain degradation coefficients (column 4).

**Table 6.** Degradation coefficients from existing fatigue models reviewed in Table 3. Note the logarithmic entropy generation  $ln \left[1 - \frac{S_{W_W}}{S_{W_F}}\right]$  derived for CDM damage [2] where load entropy  $S_{W_W} = W/T$  and  $S_{W_f}$  is the value at failure.

Measure	System Model	DEG Model	Degradation Coefficient
	$\sigma = rac{My}{T} \  au = rac{M_t y}{T}$	$\sigma = B \frac{\sigma:\dot{\epsilon}}{T}$	$egin{aligned} B_{W_{\sigma}} &= rac{MyT}{I\sigmaarepsilon}\ B_{W_{ au}} &= rac{M_{t}yT}{J au\dot{\gamma}} \end{aligned}$
Stress/Strength	$\sigma_N = rac{{\sigma'_f}^2 (4E6)^b N^b}{\sigma_e} \ \sigma_N = \sigma_0 \Big(rac{1+N/N_e}{N}\Big)^lpha$	$\begin{aligned} \tau &= B \frac{\tau \cdot \dot{\gamma}}{T} \\ \sigma_N &= B_W \frac{\sigma'_f \cdot \varepsilon}{T} \end{aligned}$	$B_{WN} = \frac{\sigma'_f{}^2(4E6)^b N^b}{\sigma_e} / \left[\frac{\sigma'_f{}:\varepsilon}{T}\right]$ $B_{W_N} = \left[\sigma_0 \left(\frac{1+N/N_e}{N}\right)^{\alpha}\right] / \left[\frac{\sigma'_f{}:\varepsilon}{T}\right]$
Strain	$arepsilon_a = rac{\sigma\prime_f}{E} \left(2N_f ight)^b + arepsilon\prime_f \left(2N_f ight)^c$	$\varepsilon_a = B_{W_N} \int_{N_0}^{N_{lef}} \frac{\dot{W}}{T} dN$	$B_{W_N} = \frac{\frac{\sigma'_f}{E} (2N_f)^b + \varepsilon'_f (2N_f)^c}{\int_{N_0}^{N_{lef}} \frac{\dot{w}}{T} dN}$
CDM Damage	$D=rac{-D_{N_{f}}-1}{lnN_{f}}ln\Big[1-rac{N}{N_{f}}\Big]$	$D = B_{W_D} ln \left[ 1 - \frac{S_{W_H}}{S_{W_f}} \right]$	$B_{W_D} = -\frac{D_{N_f-1}}{\ln N_f}$
Fracture rate	$\frac{da}{dN} = C(\Delta K_1)^m$	$\frac{da}{dN} = B \frac{(G - 2\gamma_0)j}{T}$	$B = \frac{TC(\Delta K_1)^m}{(G-2\gamma_0)j}$

In Tables 4–6, a consistent approach for obtaining DEG coefficients from existing system models was demonstrated for variegated multi-physics system transformations. The degradation coefficients can then be used to predict aging/degradation behavior and trajectory of the system as done in prior DEG publications.

# 5.4. High-Rate Processes and Multiple Simultaneous Dissipation Mechanisms

High-rate mechanical, electrical and chemical processes generate heat in the system which, in turn, raises the system's temperature. For such systems and others undergoing multiple energy transformations, the DEG theorem suggests degradation is determined from the sum of the individual contributions of all the active transformations. For materials undergoing high-rate processes accompanied by temperature rise, a thermal model should be added to the primary process model. However, for relatively steady processes or slow to average-speed processes, individual models in Tables 4–6 apply adequately and consistently.

For systems undergoing multiple concurrent interactions, a degradation coefficient is obtained for each interaction. Combined, total degradation due to simultaneously active processes is

$$\dot{w} = B_1 \dot{S}'_1 + B_2 \dot{S}'_2 + \ldots + B_i \dot{S}'_i \tag{8}$$

where *i* indexes active interactions. This renders a degradation model—which can be calibrated via pre-existing models—that weighs influence of energy changes due to individual dissipative processes. Substituting the degradation coefficients from the viscosity rows of Table 4 into Equation (8)—selecting the Mewis model for mechanical—yields total rate of degradation due to mechanical, chemical and thermal mechanisms, gauged with viscosity

$$\frac{d\eta}{dt} = \left[\frac{\eta_0 \left[exp\left(\frac{E_a}{RT}\right)\right]}{ln(T/T_0)}\right] \frac{\dot{T}(t)}{T(t)} + \left[\frac{kT(\eta_e - \eta)^n}{\tau}\right] \frac{\tau(t)}{T(t)} + \left[\frac{-\eta_0 kM_M Texp(-kt)}{\dot{m}}\right] \frac{\dot{m}(t)}{T(t)}$$
(9)

where constants C,  $\dot{\gamma}_V$  and  $\mu$  divide out. Similarly, total degradation rate via shear stress, using the Maxwell model for mechanical, is

$$\frac{d\tau}{dt} = \left[\frac{\tau_{y0}exp\left[\frac{T_0-T}{b}ln2\right]}{ln[T/T_0]}\right]\frac{\dot{T}(t)}{T(t)} + \left[\frac{TG}{\tau}\left(\dot{\gamma}-\frac{\tau}{\eta}\right)\right]\frac{\tau(t)}{T(t)} + \left[\frac{-\tau_0kM_MTexp(-kt)}{\dot{m}}\right]\frac{\dot{m}(t)}{T(t)} \tag{10}$$

The terms in square brackets can be evaluated from known properties or models of grease, or measured on samples. The coefficients determine the significance of individual dissipative processes and can be used in in situ optimization. In Equations (9) and (10), only changing values of temperature, shear stress and mass need be monitored to determine degradation rate.

#### 5.5. Unsteady Interactions

Processes with significant fluctuations render steady-state or single-process models in Tables 1–3 often inadequate for system characterization, introducing errors and inconsistency of results. As anticipated, obtained DEG coefficients will inherit the inconsistencies associated with the extent of invalidity/deviation of the used model from the actual process. For such highly unsteady interactions, which typically do not have established system models, a more detailed thermodynamic analysis employing the free energies (see Equations (A3) and (A4) in the Appendix A) was presented by the authors in recent publications (references [2,27–30]).

#### 6. Summary and Conclusions

In this study, the universal and direct applicability of the Degradation-Entropy Generation DEG theorem to interdisciplinary multi-physics system degradation analysis was demonstrated. Degradation coefficients  $B_i$  were obtained via a combination of the DEG theorem with pre-existing system-specific models. The proposed method was applied to several grease, battery and fatigue models. Using measured or existing data in the literature, system transformation/degradation behavior can be readily characterized for diagnostic and prognostic analysis.

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# Abbreviations

Nomenclature	Name
В	Degradatioin (or DEG) Coefficient
q	Charge content or capacity
F	Force
S	Entropy or entropy content
S'	Entropy generation or production
t	Time
Т	Temperature
Ε	Voltage
V	Volume
w	Degradation measure
Ν	Number of cycles or Normal force
Symbols	
σ	Stress or strength
ε	Strain
τ	Shear stress or shear strength
$\gamma$	Shear strain
η	Viscosity
μ	Chemical potential
ρ	Density
Subscripts & Acronyms	
0	Initial
f	Failure or Final
VT	Electro-Chemico-Thermal
MST, μT	MicroStructuroThermal
min	Minimum
rev	Reversible
phen	Phenomenological
DEG	Degradation-Entropy Generation
Ν	Number of cycles
W	Work or Load

#### Appendix A. Entropy Generation in Active Systems

In this section, we concisely review relevant irreversible thermodynamics concepts, from Prigogine's minimum entropy generation (Equation (A1)) and variation of entropy generation (Equation (A2)) to Osara and Bryant's phenomenological entropy generation rate (Equations (A3) and (A4)). To keep this article focused on the discussion in the main body, this Appendix A excludes detailed discussions of thermodynamics which are beyond the current scope. This paper's primary goal is to present a quick, practical and easy-to-adopt combination of entropy with existing models via the DEG theorem. We recommend to the interested reader references [2,27–30] for more on detailed derivations and breakdowns.

#### Appendix A.1. The Single-Variable System and Minimum Entropy Generation

System-process properties (or variables) often conjugate in pairs to define the system's power, e.g.,  $\sigma \dot{\epsilon}$ ,  $E \dot{q}$ ,  $F \dot{x}$ , C T,  $k \nabla T$ ,  $P v \dot{m}$  define mechanical, electrochemical, frictional/dynamic, thermal (heat storage and transfer) and flow powers, respectively. Power and energy formulations define macro transformations of systems between equilibrium states, hence are reversible. Real systems, undergoing non-equilibrium transformations, are irreversible. Theory and experiments have long established that the accuracy of energy formulations in real system characterization is higher at slow process rates: a quasi-static (very slow or nearly stationary) system is quasi-reversible. For example, cycling a battery at a high rate generates internal heat at a high rate, rendering power  $E \dot{q}$  inadequate for full characterization of the battery's transformation. This is similarly observed in other systems whose

models require temperature correction or isothermal conditions in experiments. However, many systems operate long enough to asymptotically approach steady state, during which temperature variation is minimal and therefore, negligible. Such a system undergoing a single predominant process is termed a **single-variable system** [1]. For example, steel fatigue measurements by Naderi and Khonsari [12,15] showed a pseudo-steady temperature region for most of the sample's fatigue life, prior to failure. Via temperature control, Bryant et al. [1] adequately characterized a frictional process using only the frictional work.

To measure the internal material disorganization that accompanies energy transformation in real systems, the second law introduces entropy. Generalizing Clausius' entropy—the quotient of heat transfer and temperature—to all systems, seminal works by Rayleigh, Onsager and Prigogine defined a system's *minimum entropy generation* rate as the quotient of power and temperature. Mathematically [46–48],

$$\dot{S}'_{min} = \frac{XJ}{T} \tag{A1}$$

where X is generalized force (or potential), *J* is generalized flow rate, *T* is temperature, and X/T is termed the thermodynamic force. The dot notation represents time rate of change. Equation (A1) applies to single-variable systems—systems that are minimally perturbed from equilibrium, defining the minimum condition (reference limit) for any real system to exist in nature, also known as the stationary non-equilibrium state [46,48]. The single-variable system, a pseudo steady-state system-process interaction, generates minimal entropy. Table A1 lists minimum entropy generation rate equations for various multi-physics systems.

Mechanism	Minimum Entropy Generation	
Solid Interfacial Sliding—Friction	$\dot{S}'_{min} = \frac{\eta N \dot{x}}{T}$	
Battery Cycling	$\dot{S}'_{min} = \frac{E\dot{q}}{T}$	
Heat Transfer	$S'_{min} = Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ $S'_{min} = \frac{V\tau\gamma}{T}$	
Lubricant Shearing	$\dot{S}'_{min} = \frac{V\tau\dot{\gamma}}{T}$	
Diffusion	$\dot{S}'_{min} = \frac{(\mu_{high} - \mu_{low})\dot{N}}{T}$	
Abrasion/Cutting	$\dot{S}'_{min} = \frac{F\dot{x}_c}{T}$	
Reactions (Chemical, Nuclear, etc.)	$\dot{S}'_{min} = \frac{\mu m}{M_M T}$ $\dot{S}'_{min} = \frac{V \sigma : \epsilon}{T}$	
Stress/Fatigue Loading	$\dot{S}'_{min} = \frac{V\sigma}{T}$	
Fracture	$\dot{S}'_{min} = \frac{(G-2\gamma_0)\dot{J}}{T}$	

Table A1. Steady-state or minimum entropy generation rate for multi-physics active dissipative processes.

Appendix A.2. The Thermodynamic Simple System and Phenomenological Entropy Generation

According to the thermodynamic state postulate [47,49–51], *the state of a simple system is completely specified by r+1 independent intensive properties* where *r* is the number of prevalent work interactions. To fully characterize a real system undergoing one, often unsteady, work interaction, at least two intensive properties are needed, the limit of which is the thermodynamic simple system. At steady state, the simple system reduces to the single-variable system described in Equation (A1). For example, the accuracy of Coulomb-counted charge capacity is directly dependent on the rechargeable battery's cycling rate—higher accuracy for slow cycling with minimal temperature rise [52–56].

For real systems undergoing nonequilibrium transformations, Prigogine defined the variation of entropy production [46,48]

$$\dot{S}'_{local} = \frac{J\dot{X}}{T} + \frac{X\dot{J}}{T}$$
 (A2)

where the first right-hand side term characterizes internal instabilities. Combining the first and second laws of thermodynamics with the free energies, Osara and Bryant showed that a (thermodynamic) system's free entropy generation rate [2,27–30]

$$\dot{S}' = \frac{-S\dot{T}}{T} + \frac{X\dot{J}}{T} - \frac{\dot{A}_{rev}}{T}$$
(A3)

where S is entropy content,  $A_{rev}$  is the free energy (Helmholtz or Gibbs) and other variables are as defined previously. Equation (A3) applies to all real macroscopic systems undergoing far-from-equilibrium energy transformations. The last right-hand side term in Equation (A3), the *reversible entropy rate*, can be assumed constant and defined at an initial/final reference time, and can be neglected in active system analysis. The first two right-hand side terms form the *phenomenological entropy generation rate* [2,27–30]

$$\dot{S'}_{phen} = \frac{-ST}{T} + \frac{XJ}{T}$$
(A4)

which measures a real system's instantaneous maximum work-based entropy generation rate [2,27–30]. In Equations (A3) and (A4), the first right-hand side term measures the internal dissipation effects and fluctuations that accompany unsteady processes, and the second term is the primary interaction entropy (used throughout the main article) that defines minimum entropy generation. Hence, for highly transient interactions, the minimum entropy generation, Equation (A1), is inadequate; Equations (A2)–(A4) are recommended instead. For a pseudo steady-state process or a process with minimal temperature variation  $(\dot{T} \approx 0)$  or a quasi-static—approximating a very slow—process, Equations (A2) and (A4) reduce to Equation (A1), making the latter adequate for characterizing such processes. Significantly unsteady interactions are beyond the scope of this article, hence, for more on Equations (A1) and (A2), the interested reader should consult references [46,47]. Detailed derivations and discussions of Equations (A3) and (A4) can be found in references [2,27–30].

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