A MICROSCOPIC PERSPECTIVE ON AVAILABILITY AND IRREVERSIBILITY

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ABSTRACT

A thorough understanding of the Second Law of Thermodynamics is essential for the engineer working with energy systems. How the Second Law is presented to engineering students can have a profound effect on their perception of and dependence on this fundamental principle. An alternative is described to the usual way of presenting the microscopic Second Law. This approach provides an intuitive argument separate from and supportive of the axiomatic statements of Clausius and Kelvin-Planck. The impression can then be made on the student that the Second Law describes the inherent behavior of matter and energy rather than just the functioning of heat engines.

NOMENCLATURE

e	=	energy associated with a particular level
E	=	total energy
H	=	enthalpy
n	=	population
N	=	number of members in the system
P	=	pressure
Q	=	heat
U	=	internal energy
S	=	entropy
T	=	temperature
V	=	volume
W	=	work

Greek

Ψ	=	availability
ϕ	=	irreversibility

differentials

δ	=	incremental change
Δ	=	incremental transfer
d	=	exact differential
$đ$	=	inexact differential

Subscripts

O	=	depleted state
E	=	transport out of the system (exit)
J	=	associated with level "J"
I	=	transport into the system
S	=	property of the system

INTRODUCTION

Advances in computer technology have made possible greater levels of detail and pervasiveness of analysis of thermodynamic systems. What can be done or what is being done in research facilities is becoming what is expected to be done in industry. Thermodynamic analysis of systems will be even more complex in the future as the variety of systems increases as does the economic pressure to optimize their performance.

Rather than eliminating the need for a thorough understanding of principles by relegating the task of the engineer to that of a technician or computer operator, advancing technology requires ever greater understanding on the part of the engineer. Availability and irreversibility as thermodynamic concepts rather than waning into obscurity with the rise of the computer have become standard output items on the printouts generated by thermodynamic computer codes ranging from chemical process to steam power plant models.

A thorough understanding of what availability and irreversibility are and how these are a measure of the state of a system are a must for the engineer working in the area of energy systems. The way in which these concepts are presented and the emphasis which is placed on them can have a profound impact on whether the student later considers them familiar and even indispensable principles or relatively unimportant. A microscopic perspective is essential to a proper understanding of macroscopic thermodynamic systems--especially as those systems become more complex and less resembling simple heat engines.

Many students come away from a course on macroscopic thermodynamics with the impression that the Second Law only describes the limitations of heat engines rather than the manifestation of behaviors inherent within matter and energy. Students taking an additional course on microscopic thermodynamics may not have any more understanding--especially if the text opens with statistical mechanics. Statistical mechanics is often so formidable in and of itself that the purpose for its application to microscopic thermodynamics can be lost on the student.

An alternative is offered here to the typical presentation of microscopic thermodynamics. The Second Law and the associated quantities availability and irreversibility are developed from first principles from a microscopic perspective apart from the classical dependence on heat engines and apart from an emphasis on statistical mechanics. The correspondence between the microscopic and macroscopic expressions is then shown. Statistical mechanics could then be introduced as a means by which to characterize the particles too small to see and too numerous to count which comprise energy systems.

AN ALTERNATIVE APPROACH

In a typical course on classical thermodynamics, the Second Law and the associated quantities availability and irreversibility are developed by introducing the concept of heat engines and the axiomatic statements of Clausius and Kelvin-Planck (e.g. van Wylen and Sonntag, Chapters 5-7). A typical course on microscopic thermodynamics might introduce the concepts of probability and statistical measures of state and then illustrate these for the case of an ideal gas (e.g., Pierce, Chapters 5-8). In a somewhat novel approach, Holman inserts a chapter on statistical mechanics between a classical First Law chapter and a classical Second Law one.

In teaching thermodynamics, it is important to communicate that there is a relationship between the microscopic and the macroscopic. The hypothesis which is assumed, but may not be sufficiently emphasized for the student is that macroscopic phenomena are manifestations of microscopic ones. Thus, in order to fully understand the macroscopic one must study the microscopic as well.

Furthermore, the development of the Second Law along classical lines involving heat engines may give the erroneous impression that it applies only to heat engines--unless the presentation includes the microscopic perspective. Unfortunately, even if the microscopic perspective is presented, it may be difficult to see that there is a correspondence. Perhaps the greatest obstacle is the massive subject of statistical mechanics which typically composes the bulk of the text between particle kinetics and macroscopic properties of a system. Although unquestionably essential, statistical mechanics may be a stumbling block which regrettably divorces the microscopic and macroscopic perspectives.

The alternative strategy presented here for consideration is to take particle kinetics as far as possible toward classical thermodynamics without considering statistical mechanics, then show that there is a correspondence between the two before digressing into statistical mechanics. This strategy emphasizes the general concept of the correspondence first and the mathematical means of bridging the gap second. The goal of this strategy is to prevent the correspondence from being lost in the formidable details. The first step in developing these concepts is to build a consistent foundation of thermodynamic definitions and relationships which can be applied to either microscopic or macroscopic perspectives.

Thermodynamic Systems

A thermodynamic system is an abstract conceptual tool. A thermodynamic system is a closed region in space, the extent of which is defined by the system boundary. A system boundary does not itself occupy any space and has no physical existence. A system boundary can be defined anywhere one chooses, whether realistic or not, practical or not, physically constructable or not. One is not limited as to where a system boundary can be defined; however, the choice of a system boundary greatly effects its usefulness in any analyses.

The system boundary conceptually separates the system from its surroundings. The intersection of a system and its surroundings is the null set. The union of a system and its surroundings is the entire set (viz., the cosmos). The surroundings can be divided into the immediate surroundings and the ultimate surroundings; but this distinction is somewhat artificial and must always be arbitrarily limited in some way.

There are three types of systems. An isolated system is one in which there is no transfer of energy or matter with the surroundings. A closed system is one in which there is transfer of energy, but not matter. An open system is one in which there is an transfer of both energy and matter. It is essential to emphasize that the type of system is determined solely by how one defines the system boundary (van Wylen and Sonntag, pp. 17-19).

Energy Transfer Between a System and Its Surroundings

There are three modes by which energy is transferred between a system and its surroundings: transport, work, and heat. Transport refers to the transfer of energy by virtue of the transfer of matter. Transport applies only to open systems. Work refers to the transfer of energy by the application of a force (e.g., electromagnetic or gravitational). Heat refers to all other means of energy transfer (e.g., radiation). Work and heat apply to closed and open systems.

It is important to emphasize that work and heat are only modes by which energy is transferred. Energy is a property; whereas work and heat are not properties. A system and its surroundings can contain energy; whereas they cannot contain heat or work. Heat and work only exist at a system boundary and only exist while the transfer is taking place. The sign convention used by van Wylen and Sonntag (p. 82) and Pierce (p. 186) is positive for work done by the system on the surroundings and for heat transferred from the surroundings into the system.

The First Law of Thermodynamics

The concept of energy is inseparably linked to the First Law of Thermodynamics. The First Law is deduced from observations and can be stated as follows: there is a property (energy) that is conserved or remains constant in any process or interaction.

For an isolated system there is no transfer of energy with the surroundings. Therefore, the energy of an isolated system is constant. Denoting a change in the energy of the system by δE_S, this relationship can be expressed by Equation 1.

$$\delta E_S = 0 \tag{1}$$

For a closed system the only means of energy transfer are work and heat. Denoting an incremental transfer of heat by ΔQ and work by ΔW, this relationship can be expressed by Equation 2 (van Wylen and Sonntag, p. 96).

$$\delta E_S - \Delta Q + \Delta W = 0 \tag{2}$$

For an open system energy is transferred by means of transport, work, and heat. Denoting an incremental transport into and out of the system by δE_I and δE_E respectively, this relationship can be expressed by Equation 3 (van Wylen and Sonntag, p. 124).

$$\delta E_S - \Delta Q + \Delta W - \delta E_I + \delta E_E = 0 \tag{3}$$

Availability and Irreversibility

Energy is often incorrectly defined as the potential for doing work; whereas, availability more nearly fits this definition. More specifically, availability is the maximum energy which can be transferred between a system and its surroundings in such a way as to theoretically extract work (van Wylen and Sonntag, p. 282). Whether or not such a maximum extraction of work is possible introduces the concept of irreversibility. Irreversibility is defined as the difference between the ideal maximal and actual work extraction

for a process. Denoting a change in availability by $\Delta \psi$ and irreversibility by $\Delta \phi$, this relationship can be expressed by Equation 4 (van Wylen and Sonntag, p. 276).

$$\Delta \phi = -\Delta \psi - \Delta W \geq 0 \tag{4}$$

The negative signs in the above expression arise from the sign convention for work being opposite of that for transport and heat transfer.

Because availability is the theoretical maximum, $-\Delta \psi$ must always be greater than or equal to ΔW. Thus, $\Delta \phi$ must always be greater than or equal to zero. It is important to emphasize that this inequality which relates irreversibility to availability and work is not an empirically deduced principle--as is the First Law--it is a definition. It will be shown subsequently that this expression for a change in irreversibility, $\Delta \phi$, is actually the Second Law. Expressions for the work, ΔW, are straightforward. What remains to be developed are expressions for the change in availability, $\Delta \psi$.

Energy is a property of a system, and as such depends only on the state of the system. Availability is based on ideal maximal work, which implies an interaction with the surroundings. Thus availability depends on the state of the system and its surroundings. It is intuitive that both measures are necessary; because there are many systems which contain significant energy, but which seem incapable of doing any work. It is also intuitive that the availability of a system depends on its relation to the surroundings. For example, a tank containing air at room temperature and 1 bar has little or no availability. However, if the atmospheric pressure were only 0.5 bar, the same tank of air--all other things being equal--would have availability to, for instance, drive a turbine.

Partitioning of Energy within a System

Central to the understanding of availability is the concept of energy partitioning; or how the energy is distributed within a system. In a system there are a finite multitude of attainable energy levels; and within each energy level there can be a number of states which have the same energy (Pierce, p. 157). Not all energy levels are attainable by a system. For instance, a level which exceeds the energy of the entire system would not be attainable. Furthermore, not all energy states within a level are attainable. Although the population of a level may be large, the Pauli Exclusion Principle asserts that the population of a unique energy state is limited to no more than one (Pierce, p. 170). Quantum theory asserts that the attainable energy states and thus levels can assume only discrete values (Pierce, p. 166).

Consider an isolated system containing N irreducible, distinct, although not necessarily distinguishable, members (N need not be large). The system has attainable energy levels, e_J. The population of each level is n_J. The populations, n_J, need not be large (typically many of the attainable energy levels in a system are empty). Two of the constraints on the system are the conservation of members;

$$\sum n_J = N \tag{5}$$

and the conservation of total system energy (Pierce, p. 136).

$$\sum n_J e_J = E_S \tag{6}$$

For example, consider a system containing 3 members (abc) and having 5 discrete attainable energy levels (0-4) and a total system energy of 4, there are 15 different attainable partitionings (A-O) as illustrated in Table 1 (Pierce, p. 129).

Table 1. Energy Partitionings

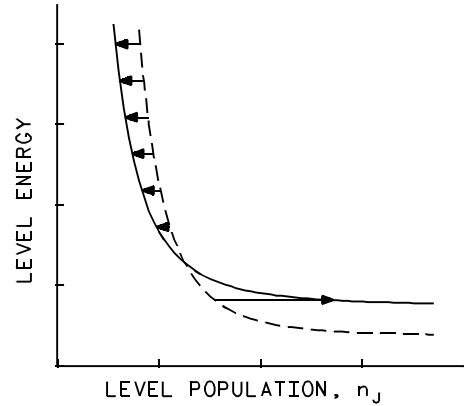| | energy levels | | | | |
partitioning	0	1	2	3	4
A	ab				c
B	ac				b
C	bc				a
D	a	b		c	
E	b	a		c	
F	a	c		b	
G	c	a		b	
H	b	c		a	
I	c	b		a	
J	a		bc		
K	b		ac		
L	c		ab		
M		ab	c		
N		ac	b		
O		bc	a		

Changes in Population and Attainable Energy Levels

Consider an arbitrary change in the total energy of a system, δE_S, with populations and levels as indicated by Equation 6. This change in energy is given by:

$$\delta E_S = \sum e_J \delta n_J + \sum n_J \delta e_J \tag{7}$$

The first term, $\sum e_J \delta n_J$, represents a change in energy due to a redistribution of populations. The second term, $\sum n_J \delta e_J$, represents a change in energy due to a change in energy levels. These changes are illustrated in Figures 1 and 2 respectively (Pierce, pp. 184-186).

An analogy which is helpful in understanding the changes illustrated in Figures 1 and 2 is that of parallel dams on parallel rivers, each with a different elevation (not series dams on a single river). In this

Figure 1. Change in Energy Levels
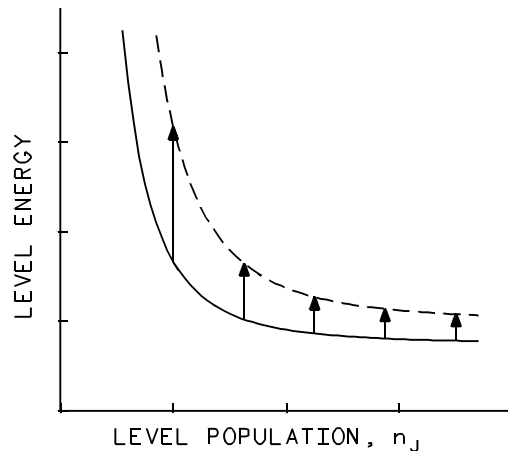
Figure 2. Change in Energy Levels

illustration energy level is analogous to elevation and population is analogous to volume. The change in Figure 1 is analogous to exchanging sediment from the upper reservoirs for water from the lower such that the elevations and the total volume of water remain constant. As a result of this change there is more volume in the upper reservoirs and less in the lower. The change in Figure 2 is analogous to increasing the total sediment in the reservoirs such that the elevations increase, but the total volume of water remains constant. In both cases the energy of the system is increased by raising the center of gravity of a constant volume of water. However, in the first case, the attainable hydro power remains constant; whereas in the second case it increases.

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The process in Figure 1 is a redistribution of populations within the same levels; thus there is no useful work associated with this process. The process in Figure 2 is a change in levels with the populations locked into each level. Useful work could be extracted to the surroundings as levels drop or input to the system as levels increase (Pierce, p. 185).

Availability and the Depleted State

As stated previously, expressions for the availability of a system must necessarily consider the state of the system and the state of the surroundings. For the purposes of thermodynamic analysis it is necessary to distinguish between the immediate and ultimate surroundings. Thus it is assumed that the immediate surroundings of a system can, at any given instant, be characterized in some way by energy levels and populations as implicitly assumed for the system. Furthermore, it is postulated that, at any given instant, there exists a "depleted state" of the system with respect to the immediate surroundings such that the system in that state will have zero availability (viz. unable to do any more useful work unless the state of the immediate surroundings changes).

This depleted state is designated by the subscript "0" (zero). The corresponding energy of the system is designated by E_{S0}, populations, n_{J0}, and levels, e_{J0}. This "depleted state" is not "absolute zero" or zero energy (i.e., e_{J0} are not necessarily zero). The "depleted state" is depleted relative to the immediate surroundings, not "absolutely depleted".

The difference between a change in energy and one in availability is called the "unavailable energy". Returning to the dam analogy, the "unavailable energy" is the energy associated with the volume below the turbine inlets. The "unavailable energy" for a dam is equal to the product of the elevation of the turbine inlet and the change in the corresponding volume of the reservoir. The microscopic equivalent of this "unavailable energy" is equal to the product of the depleted energy level and the change in the corresponding population or, $e_{J0}\delta n_J$. Subtracting this change in "unavailable energy" from the total change in energy (Equation 7) yields Equation 8 for the change in availability.

$$\Delta\psi = \sum(e_J\text{-}e_{J0})\delta n_J + \sum n_J\delta e_J \qquad (8)$$

The first term in Equation 8 accounts for the redistribution of populations and the second term for the change in energy levels from the present to the depleted state. Using the dam analogy, e_J and e_{J0} are the initial and final elevations respectively and n_J and n_{J0} the initial and final volumes respectively for reservoir

"J". The first term is the elevation difference times the change in volume for each reservoir; and the second term is the volume times the change in elevation for each reservoir. Recognizing that $\delta e_{J0} = 0$, Equation 9 can be differentiated to obtain Equation 8. Therefore, Equation 9 is the microscopic equation for the availability of a closed system.

$$\psi = \sum(e_J\text{-}e_{J0})n_J \qquad (9)$$

Thus the availability of a closed system is equal to the sum of the product of the present populations and the difference between the present and depleted energy states. This expression also follows intuitively from the dam analogy.

Equations 3 and 9 can be combined to give the microscopic equation for the availability of an open system.

$$\psi = \sum(e_{SJ}\text{-}e_{SJ0})n_{SJ}\text{-}\sum(e_{IJ}\text{-}e_{IJ0})n_{IJ} + \sum(e_{EJ}\text{-}e_{EJ0})n_{EJ} \qquad (10)$$

Here the additional subscripts S, I, and E have been added to distinguish between the system, transport into, and out of (exiting) the system respectively.

Consider the system described in Table 1 with an initial state of A and a depleted state of Z. In state Z consider the energy levels to have dropped from 01234 to 00112; and the populations to have changed from 20001 to 11100. The energy excess relative to the depleted state would be:

$$E\text{-}E_0 = (2\times 0 + 0\times 1 + 0\times 2 + 0\times 3 + 1\times 4)$$
$$-(1\times 0 + 1\times 0 + 1\times 1 + 0\times 1 + 0\times 2) = 3$$

The availability would be:

$$\psi A = 2\times(0\text{-}0) + 0\times(1\text{-}0) + 0\times(2\text{-}1)$$
$$+ 0\times(3\text{-}1) + 1\times(4\text{-}2) = 2$$

If the initial state had been D rather than A the excess energy would be the same; but the availability would be:

$$\psi D = 1\times(0\text{-}0) + 1\times(1\text{-}0) + 0\times(2\text{-}1)$$
$$+ 1\times(3\text{-}1) + 0\times(4\text{-}2) = 3$$

Similarly for initial states J and M respectively:

$$\psi J = 1\times(0\text{-}0) + 0\times(1\text{-}0) + 2\times(2\text{-}1)$$
$$+ 0\times(3\text{-}1) + 0\times(4\text{-}2) = 2$$

$$\psi M = 0\times(0\text{-}0) + 2\times(1\text{-}0) + 1\times(2\text{-}1)$$
$$+ 0\times(3\text{-}1) + 0\times(4\text{-}2) = 3$$

The microscopic expression for the change in irreversibility of a closed system can now be obtained

by substituting Equation 8 into Equation 4 to yield Equation 11.

$$\Delta\phi = -\sum(e_J - e_{J0})\delta n_J - \sum n_J \delta e_J - \Delta W \geq 0 \qquad (11)$$

Similarly, the expression for an open system can be obtained in the same way using Equation 10.

$$\Delta\phi = -\sum(e_{SJ} - e_{SJ0})\delta n_{SJ} - \sum n_{SJ}\delta e_{SJ}$$
$$+ \sum(e_{IJ} - e_{IJ0})\delta n_{IJ} + \sum n_{IJ}\delta e_{IJ}$$
$$- \sum(e_{EJ} - e_{EJ0})\delta n_{EJ} - \sum n_{EJ}\delta e_{EJ} - \Delta W \geq 0 \qquad (12)$$

CLASSICAL THERMODYNAMICS

Equations 11 and 12, although not in their most familiar forms, are the Second Law of Thermodynamics for closed and open systems respectively. In developing these equations no mention has been made of pressure, temperature, entropy, or heat engines--all macroscopic concepts. It will now be shown that the above microscopic expressions have a direct correspondence to the classical macroscopic expressions.

Equation 7 is the change in energy for a closed system. Only the second term, $\sum n_J \delta e_J$, contributed to the ideal work of the system. For a simple stationary classical system where only the internal energy, U, is significant and the only means of exchanging work with the surroundings is mechanical, the ideal work performed on the system is given by Equation 13 in terms of the pressure, P, and the volume, V (van Wylen and Sonntag, p. 70).

$$-\text{đ}W_{IDEAL} = -PdV \qquad (13)$$

Therefore, these two terms must be equal.

$$\sum n_J \delta e_J = -PdV \qquad (14)$$

Here the distinction is made between exact differentials (i.e., properties of the system) and inexact differentials (i.e., work and heat) by the two symbols for differentiation, d and đ, respectively.

The classical expression of the First Law for a closed system which can be taken as one definition of entropy, S, and involving the temperature, T, is given by Equation 15 (van Wylen and Sonntag, p. 212).

$$dU = TdS - PdV \qquad (15)$$

For this system $dU = \delta E_S$; therefore, the second term in Equation 7 must be equal to TdS.

$$\sum e_J \delta n_J = TdS \qquad (16)$$

Furthermore, the second term in Equation 8 must be equal to $T_0 dS$.

$$\sum e_{J0}\delta n_J = T_0 dS \qquad (17)$$

Which means that Equation 11 must be equivalent to Equation 18.

$$\phi = -(T - T_0)dS + PdV - \text{đ}W \geq 0 \qquad (18)$$

Adding Equations 2, 15, and 18 yields Equation 19.

$$\phi = T_0 dS - \text{đ}Q \geq 0 \qquad (19)$$

which is the classical expression of the Second Law for a closed system (van Wylen and Sonntag, p. 277). The differential availability can be found by adding Equations 2 and 4 and subtracting Equation 19.

$$\Psi = dU - T_0 dS \qquad (20)$$

which is the classical expression for the availability of a closed system (van Wylen and Sonntag, p. 283). Similarly, Equation 12 can be used to determine corresponding expressions for an open system.

$$\phi = T_0 dS_S - T_0 dS_I + T_0 dS_E - \text{đ}Q \geq 0 \qquad (21)$$

$$\Psi = (dU_S - T_0 dS_S) - (dH_I - T_0 dS_I) + (dH_E - T_0 dS_E) \qquad (22)$$

Here in the case of an open system, enthalpy, H, is the appropriate measure of energy for the inlets and exits.

SUMMARY

The preceding derivations show that microscopic expressions for availability, irreversibility, and the Second Law can be developed apart from references to heat engines. Thus, reinforcing the concept that these are not restricted to heat engines. This also reinforces the veracity of the Clausius and Kelvin-Planck axioms.

The similarity and correspondence of the microscopic and macroscopic relationships illustrates that there is an equivalence of the two perspectives and reinforces the hypothesis that macroscopic phenomena are manifestations of microscopic ones.

The impression is also given that if one were somehow able to characterize the energy of every member of a system, then one could compute classical thermodynamic properties from particle kinetics as illustrated for the system in Table 1. This is also a logical point at which to introduce statistical mechanics as a means to solve the logistical problem of systems

composed of members too small to be seen and too numerous to be counted.

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