

Extending Thermodynamic Concepts from the microscopic nonliving system to the macroscopic living system

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Abstract

This paper summarizes some key questions arising in a seminar discussion of thermodynamics and its application to living systems. The seminar began with a discussion of fundamental questions related to: thermodynamic systems, energy, temperature, heat, exergy, entropy, work and state equations. The seminar considered thermodynamic laws and thermodynamic equilibrium from classical and modern viewpoints. The context of the discussion was focused around living systems. Referenced resources comprised the readings list.

Introduction

This discussion seminar stemmed from the proposition that thermodynamic laws guiding nonliving and living processes drive ecological processes. We set about to review and refresh ourselves on the thermodynamics of nonliving processes in order to provide orientation from which to begin an inquiry into the thermodynamics of living systems. Several questions were surfaced and the answers that evolved over the course of the discussion are presented.

A. What is a thermodynamic system?

A thermodynamic system, or system, from a macroscopic viewpoint is defined as a quantity of matter or a region in space chosen for study. The mass or region outside the system is called the surroundings (Cengel and Bowles, 2002, page 8-9, 168) or the environs (Patten, 1978). The real or imaginary surface or line that separates the system from its surroundings is called the boundary, which may be fixed or moveable.

A closed system, known also as a control mass, consists of a fixed amount of mass and no mass can cross its boundary. Energy in the form of work or heat can cross the boundary. If energy is not allowed to cross the boundary, the system is referred to as an isolated system.

The closed system does not allow mass transport through boundaries but may allow energy transport. Closed systems with no chemical reactions or phase changes, whose velocity and elevation of the center of mass remains constant are referred to as stationary systems. In a stationary system, a change of energy represents a change in sensible internal energy, with kinetic energy changes requiring complementary changes in potential energy. In the event of chemical reactions and phase changes, one must consider latent energy and chemical internal energy as contributors to the energy state. System boundaries allowing no heat transfer are known as adiabatic boundaries.

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An open system, or control volume, is a properly selected region in space. It usually encloses a device that involves mass flow. The boundaries of the control volume are called the control surface. Energy and mass transport are possible and are treated as conserved quantities. Entropy (discussed later) is not conserved in practical thermodynamic systems.

Elegant mathematical approaches of vector calculus and tensor analyses have been motivated by the need to study systems on the differential level. Eulerian and Lagrangian (moving volume) analyses approaches are used, with Eulerian (fixed volume) approaches being perhaps the most common. At the next scale up the integral approach to the various conserved quantity relationships (e.g., mass, energy, momentum, etc.) are commonly used. The Reynolds transport theorem underlies most macroscopic analyses. The common continuity equation ($Q=AV$) follows directly from the Reynolds transport theorem and is perhaps the most often used conservation relation at the macroscopic level. Our emphasis here is concerned with energy and mass (as a carrier of energy).

System definition is fundamental to a rigorous study of the thermodynamics of nonliving and living bodies. Living systems frequently include a portion of the environment around the living entities. Creative definition of the system can greatly affect the ease or difficulty of solving a problem of interest. Failure to define clearly the system and boundary properties leads to an imprecise and improper discussion of systems, which explains many difficulties in thermodynamic problem solving.

B. What is energy?

Energy is a virtual concept and provides the central unifying concept for any discussion of energetics. Energy is frequently considered limited; however, the universe of energy is practically unlimited. The question is to find the energy in a form that is compatible with our technology. Total energy to a system represents contributions of mechanical potential energy, mechanical kinetic energy, thermal energy (internal), exergy, entropy, work and chemical energy, including phase changes (other forms of internal energy), electrical energy, and possibly other energy modalities. We discuss several of these modalities of energy transfer in additional detail below

Energy represents the capacity to do work. Energy is conserved and conversions to and from the various modalities depend on the system. Cengel and Bowles (2002) give several applications of the energy balance in closed and open systems. The smallest possible quantum of energy transfer is that represented by Plank's constant.

An interesting feature of energy is that each form of energy is calculated from a reference state. The reference may be chosen to facilitate solution. Energy does not depend on the scale. Movements of the center of mass may be added to the movements of particular particles to get total mechanical energy, for example. Similar additions are possible for other energy bearing modalities, particularly if the potential difficulties with defining temperature in the context of purposeful movement are ignored.

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Energy is frequently viewed as an entity that is limited in supply and that must be conserved at all costs. This limited view of energy is contrary to what is observed in the universe. It indeed seems that energy is practically unlimited in time and space. Because energy is required to drive the open ecological system, this is indeed comforting.

C. What is temperature and heat?

The concept of temperature is rich in interpretations and levels of abstraction. In its anthropomorphic understanding, temperature is a measure of the hotness of a given macroscopic object (Zemansky and Dittman, 1997, page 10). The homemaker thinks of temperature as how hot she must set the oven to cook a roast. The computer engineers think in terms of how cool a computer system must be maintained in order to function properly. The plasma physicist views temperature as a measure of kinetic energy of the molecules or electrons. The astronomer views temperature as a measure of the radiant energy emission from stars. These rather diverging concepts of temperature have one thing in common: they all relate to energy or energy transfer and hence clearly mark temperature as a thermodynamic property (Reynolds, 1968).

The Carnot engine provides the working definition of the thermodynamic temperature scale because the efficiency of the Carnot engine depends only on temperature, regardless of the working media (Zemansky and Dittman, 1997, page 177). The convergence of the triple point of water temperature to be 273.16K with the gas thermometer and the fact that heat removal ratios are function of temperature as measured from some zero point secures the basis for measuring thermodynamic temperature.

Microscopically, the translational and rotational energies associated with molecules and elements are minimum at zero absolute temperature. The notion that all molecular motion ceases is not strictly valid because, from a quantum mechanics standpoint, sub molecular particles do not cease moving and possess a finite amount of vibrational energy known as the zero-point energy (Zemansky and Dittman, 1997, page 20).

Adding the notion of motions of larger entities such as individual species may complicate the concept of temperature by adding purposeful motions to the random motions of molecules and elements. This difficulty must be held open as one adds living entities to the thermodynamic systems under considerations. The fact that the first law of thermodynamics (discussed below) is generally regarded to hold, with inclusion of heat energy, requiring a definition of temperature, may mean that the addition of purposeful movement to the molecular movements does not greatly change the overall temperature context.

D. What is exergy?

Exergy is the portion of energy that can do useful work in a given context. For example with the total heat energy moving through a system, an amount not to exceed the Carnot efficiency can provide useful work. Exergy is a relatively recent addition to the suite of

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energy nomenclature. What we now call exergy used to be handled simply by differencing the total energy and the temperature-entropy product, which represents non-useful energy to the system.

The difference between kinetic and potential energy (called the Hamiltonian) represents mechanical exergy and is useful in defining conditions of mechanical equilibrium. The first three terms of the Gibbs function, defined as $G=U+PV+\sum\mu -TS$ represent exergy, with U representing internal energy, PV (Pressure*Volume) represents pressure potential, and μ represents chemical potential and TS represents a product of temperature and entropy. The TS product represents the portion of energy that is not available, or, exergy destruction. The exergy terms define Lyapunov functions, as do other functions described below that can be formed from ecological orientors. The Lyapunov function, discussed by Kreider, et al. (1968) enables an important bridge from quantitative measures of classical exergy to the more speculative ecological orientors in that Lyapunov functions may be written for these as well. These similarities (further discussed below) provide some support for the notion that the orientor is a useful concept for describing thermodynamic coordinates in the ecological context.

If energy is truly unlimited as speculated above, then one may also argue that exergy is unlimited as well. Exergy is not conserved; it is destroyed as entropy is produced. Exergy is not an additive parameter in that, with each particular energy modality, the partition between useful and nonuseful energy is context dependent (Svirezhev, 2001a).

The formula for computing the Gibbs energy of a particular material with a phase difference is frequently used to estimate energy or exergy based on zero mechanical energy. The relationship appears as $G= (RT/w) \ln(C_2/C_1)$ where R is the gas constant, T is absolute temperature, w is molecular weight, C_2 is the final concentration, and C_1 is the initial reference concentration. The relationship is considered as somewhat imprecise in that 1) the reference concentration is a self-reference and somewhat arbitrary; 2) the final concentrations are frequently separated from the processes originating from initial concentrations over many years; and 3) the nature of the coordinate system with potentially many zones of local equilibrium may render the expression invalid for these complicated situations due to the need for activation energy to enable movement from a given site of local equilibrium. These conditions suggest that exergy calculations by authors such as Jorgensen (2001) should be regarded as order-of-magnitude at best. The same statement would apply to some of the energy computations by Odom (1996).

E. What is entropy?

Not all energy is available to do work. The portion of energy that is theoretically available for doing work is referred to as exergy. The destruction of exergy is synonymous with the production of entropy. Entropy, a virtual quantity, is defined as $\Delta Q/T$. A process is defined as reversible if the summation of $\Delta Q/T$ is zero, thus Entropy is zero around a cyclical process. Energy not available to do work is defined as $T\Delta S$. Entropy is not a conserved quantity. Entropy is generated in practical closed and open systems, meaning that entropy is not a conserved quantity.

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Cengel and Bowles (2002) provide several examples of the entropy balance, showing the entropy generation term. The portion of energy that is useful is commonly denoted as exergy. Heat exergy is that work that can be done by the Carnot engine.

From a microscopic perspective, a reversible system must, on a particle-by-particle basis, be reversible in time, path and experienced forces. This is quite impossible. The notion of reversibility enables exact differentials that provide very powerful mathematical relationships. The microscopic definition of entropy is related to a summation of variances representing deviations from an equilibrium state (De Groot and Mazur, 1983). This definition is related to the Boltzmann definition of entropy in terms of the thermodynamic probability.

De Groot and Mazur (1983) discuss the mass, energy and entropy balance from a mathematically rigorous viewpoint. They provide equations for the entropy flux in processes with simultaneous momentum, diffusion, thermal and electrical transport. Entropy flux is the common denominator for the discussion. Entropy is the basis on which the Onsager coefficients are developed. The Onsager coefficients enable relations for example of simultaneous heat and mass transfer modalities in a quasi-static state. As the systems moves from near equilibrium to far-from equilibrium conditions, higher order terms in the transport relations become necessary to describe mass, momentum, energy, electrical and other transport modalities. This implies that Fourier's law of heat conduction, Stokes law of momentum transfer, Ohm's law of current flow, Fick's law of diffusion, for example are not adequate to describe mass transport in a system substantially away (the definition of "substantial" is left to the investigator) from equilibrium. Entropy as discussed above was concerned with entropy transport over the boundaries in the form of heat or mass. As such is general seen from an external standpoint, except for the entropy generated.

Svirezhev (2001) posits that, for the open system, one may partition entropy into an equilibrium component, external component and internal component. (See Jorgensen, 2001, page 122 for this discussion). The equilibrium component is the entropy calculated from a standard condition. (Zemansky and Dittman, 1997) discuss this calculation at length. The external component represents the quasi-static push from equilibrium, where it is assumed that all transport laws in linear form apply. The internal form is the second order term. Svirezhev (2001a) seems to imply that the second order contribution represents a life contribution. He shows that this term satisfies a Lyapunov function also related to the variances of thermodynamic coordinates. The nature of the coordinate system is a subject of debate with living systems, as is the nature of Svirezhev's (2001a) partition. Lyapunov functions are further discussed under the equilibrium heading below.

There is a fundamental difference between the entropy of classical mechanics and the entropy discussed in conjunction with systems containing living systems. The entropy of the classical system is estimated using the Boltzmann approach that relates entropy to the thermodynamic probability. Zemansky and Dittman (1997, page 311) discuss the computation of the thermodynamic probability for the ideal gas. They also discuss the

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computation of the thermodynamic state in metals and nonmetals. Degeneracy (the number of quantum states having the same total energy) varies with the material classification and must be decided based on quantum mechanics considerations. A common assumption of weak particle-particle interactions is also made. Computing the entropy in a system with life-bearing components from a microscopic view is complicated by our lack of ability to compute the thermodynamic probability in a classical sense. As discussed under the temperature heading, the addition of purposeful motion to the random motion of particles coupled with the possibility of both strong and weak interactions complicates the picture.

The most common approach to entropy like computations in ecological systems borrows from information theory, after computing macroscopic ratios that behave like probabilities. The Shannon-Weaver information theory is patterned after the Boltzmann definition of entropy. Patten (1978), Ulanowicz (2000), and Svirezhev (2001b) provide details. It is interesting to speculate that these macroscopic computations may embody the Svirezhev (2001a) internal and external entropy components. The similarities of the Boltzmann definition of entropy with the information theory approaches and the similarities of the Lyapunov relation associated with Svirezhev's (2001a) concept of internal entropy being a second order effect makes for interesting discussion but does not resolve the debate as to what entropy is on the ecological scale. It is further interesting to note that Aoki (2001) has made much use of the concept of external entropy (e.g., the customary macroscopic approach) in his study of ecological systems. The fundamental debate regarding the entropy contribution of the life-bearing portion of a system renders it difficult to reduce living systems to an inanimate physical simulation.

F. What is degradation and dissipation of energy?

Degradation is a general term that refers to the reduction of the ability to recover useful work from a given energy level, accompanied by a loss of temperature. The Carnot efficiency represents the most work that one may possibly recover from material at a given temperature moving toward a lower temperature. Dissipation is the energy in the form of heat that is lost from a closed system. Dissipation crosses the system boundary in the form of heat that is contained in neither in the input stream or output stream of an open system. Dissipation is one of the possible forms of heat crossing the boundary of a closed system between initial and final state attainment. Dissipation, entropy generation and exergy destruction are synonymous in closed and open systems. In an isolated system, energy degrades but does not dissipate because energy is not lost from the isolated system.

G. What is work?

Work is the product of force and displacement parallel to the force. As with other parameters, elegant vector and tensor mathematics may be used to describe work when the force is not parallel with the displacement. Work has units of energy. If a system as a whole exerts a force on its surroundings and a displacement takes place, the work that is done by or on the system is called external work. Work done by one part of a system on

another part of the system is known as internal work. The interactions of molecules, atoms or electrons on one another constitute internal work. (One may also add life-bearing entities to this definition of internal work). Zemansky and Dittman (1997) define the work modes for several thermodynamic systems. Work is a key mode of interacting with a nonliving system.

The notion of doing work on a living system is somewhat problematic. In the context of a living system, one usually defines the system to contain the environment around the life bearing entities and does work on the environment. Living entities perform work function within a living system. This internal work would probably best be treated as internal energy.

H. What is an equation of state?

The equation of state provides a relationship among the relevant thermodynamic coordinates describing a system. For example, the gas law describes the ideal compressible substance, with pressure, volume and temperature being the relevant coordinates. Zemansky and Dittman (1997) provide other examples regarded as canonical in the nonliving context. The equation of state is not to be confused with the constituent conservation relationships such as mass, energy and momentum conservations.

When moving to living systems, the selection of thermodynamic coordinates becomes a debatable issue. The thermodynamic definition of temperature is debatable. Other thermodynamic coordinates relevant are also under debate. The concept of the ecological orientor may provide a basis for defining some of the coordinates in the ecological context. Bossel (2001) provides much discussion relative to the orientors. With appropriate metrics, these may play into the Lyapunov function approach for describing ecological systems. Similarities in the form of the internal entropy definition and the resulting Lyapunov function written with various orientors lends some credence to the orientor approach. Network theory as described by Patten (1978) may also enable the identification of appropriate parameters and relationships among relevant the parameters to provide the equivalent of an equation of state for given systems. Unlike the canonical physical systems studied, the state relationships for ecological systems will likely be more site specific.

I. What are the fundamental laws of thermodynamics?

Zeroth law: Two systems in thermal equilibrium with a third system are in thermal equilibrium with each other. The discussion of temperature underlies this discussion. Note that some authors refer to the zeroth law as the third law. Jorgensen (2001) analyses the numbers of observations needed to characterize an ecological system from an individual particle consideration and concludes the task to be impossible.

It is interesting to speculate on what the zeroth law means in the ecological context, where the association to temperature with motion may become harder to describe.

First law: The first law is formulated to represent three ideas:

- 1) the existence of an internal energy function, where internal energy may be due to temperature induced molecular movement, latent energy expressed in phase changes, or latent chemical energy expressed in chemical reactions;
- 2) the principle of conservation of energy (and mass); and,
- 3) the definition of heat as energy in transit by virtue of a temperature difference.

Closed system: When a closed system whose surroundings are at a different temperature and on which mechanical work may be done undergoes a process, then the energy transferred by non-mechanical means, equal to the difference between the change of internal energy and the mechanical work is called heat. Latent (phase change) and chemical energy are treated as components of the internal energy.

Open system: The first law as applied to the open system says that the net energy change relative to the system boundaries is equal to the change of energy per unit time within the system. If the net change within the system is zero, the system is said to be in steady state if the inputs and outputs are also not changing with time. One usually analyses the open system using rate units. Cengel and Bowles (2001) provide some excellent examples of first law analyses.

There seems to be broad consensus that the first law is generally applicable to ecological systems of all scales. The ease of defining energy across a broad range of spatial and distance scales makes this possible.

Second law: The second law states that the net entropy generated in a process is equal or greater than zero. Zemansky and Dittman (1997) discuss the Clausius (impossible to construct a refrigerator requiring less work than that associated with the heat being transferred from a cold to a hot thermal energy reservoir) and Kelvin-Planck (impossible for a heat engine to do more work than the equivalent heat transferred from a hot to a cold thermal energy reservoir) variations of the second law. Both these variations essentially state that the perpetual motion machine is impossible. The reversible process generates zero entropy. Cengel and Bowles (2001) provide excellent examples of second law analyses with and without chemical reaction in nonliving systems. They consider isolated, closed and open systems. Entropy and second law analyses dictate the direction of a process. These concepts are also important in the notion of goal functions, further discussed below.

The introduction of living entities in a system complicates the estimation of entropy from a microscopic sense. The macroscopic balance is still regarded as valid, with the entropy generation term being the impacted parameter. Aoki (2001) gives an excellent summary of efforts to compute macroscopic entropy balances in ecological systems.

Other laws: Additional laws of thermodynamics particular relevant to the ecological context have been proposed. For example, Odum (1996) proposed the maximum empower principle as the fourth law and the energy transformation hierarchy as the fifth law (note that he regards the zeroth law as the third law). The fifth law of

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thermodynamics states that a surplus of exergy over time will lead to increasingly higher concentrations of exergy; or the steady growth of a gradient between equilibrium and nonequilibrium conditions.

The maximum empower (see Odum, 1996) principle builds on his concept of emergy, which in turn builds on the total solar energy embodied in an entity. The maximum empower principle says that a process will destroy emergy at the maximum rate possible. This represents a goal function, a concept that is further discussed below. The energy transformation theory (Odum, 1996) says that energy flows in the universe is organized into energy transformation hierarchies. This theory builds on ideas traced back to Lotka. Jorgensen (2001) traces this idea back to the notion that energy, when flowing in processes far from equilibrium, organizes themselves to form ordered structures.

The acceptance of the fourth law of thermodynamics implies a practically unlimited supply of energy in the universe. It should be noted that the veracity of the qualitative correlation between exergy excess, time and appearance of higher life forms is not tested.

Jorgensen (2001) notes that the Odum (1996) fifth law [the 4th law of Jorgensen (2001)] law of thermodynamics makes it possible to unify the maximum empower (and maximum power) hypothesis and the minimum energy hypothesis traced back to Prigogine. The hierarchical organization of species implies to many that ecological systems are far from equilibrium. The integration of the ecological scale into the customary thermodynamic continua may bring additional laws. Thermodynamics is thus an evolving discipline and not a static, fully developed discipline.

Additional thoughts: Introducing the notion of a living entity into the thermodynamic system poses some interesting problems and sets interesting parameters. In the worst case, uncertainties regarding the definition of temperature, the microscopic definition of energy, the definition of entropy inject uncertainty concerning how to write balances that satisfy the laws of thermodynamics. The proper choice of coordinates is debatable. The question of nearness or farness from equilibrium also figures into the mix of uncertainty. In the best case, temperature is identical to the microscopic temperature. One may also identify thermodynamic coordinates. Entropy may be estimated macroscopically or using information theory-based approaches.

J. What is meant by thermodynamic equilibrium and how is it assessed?

The notion of equilibrium has run throughout this discussion. The following statements define the common usage of the term “equilibrium” (Webster’s 7th New Collegiate Dictionary):

1. a static or dynamic state of balance between opposing forces or actions.
2. a state of adjustment between opposing or divergent influences or elements.
3. the normal oriented state of the animal body in respect to its environment.

The dictionary definitions allow for overlap between the notion of a steady state (e.g., the system parameters are constant with time) and the requirement of no motion. The usage of the term in a thermodynamic sense is more stringent (Zemansky and Dittman, 1997, page 50):

Mechanical equilibrium: There are no unbalanced forces or torques acting on any part of the system or the system as a whole.

Thermal equilibrium: There are no temperature differences between parts of the system or between the system and its surroundings.

Chemical equilibrium: There are no chemical reactions within the system and no motion of any chemical constituent from one part of a system to another part.

The notion of equilibrium may be extended to other modalities such as electrical equilibrium, which would imply no potential differences relative to an arbitrary ground state anywhere in the system, thus no charge displacements.

The concept of equilibrium does not extend to the microscopic statistical mechanics level. Molecular and atomic motion is permitted. Even at absolute zero, where most molecular and atomic motion ceases, motion is permitted at the subatomic level.

The thermodynamic definition of equilibrium does not admit steady state condition but the more stringent condition of no macroscopic movement. One must first clearly define the system prior to any consideration of equilibrium. An isolated system is in equilibrium at a point of maximum entropy. A closed system (receives energy but no mass moves through the boundary) or an open system (mass and energy move through the boundary) do not come to strict thermodynamic equilibrium, although they are close to equilibrium. The slight deviation of equilibrium, and resulting continual entropy generation, require one to adopt a modified view of the maximum entropy production precept (attributed originally to Clausius). A closed or open system approaches a state of minimal entropy generation rate as it goes as close to thermodynamic equilibrium as possible (articulated by Prigogine). Closed or open systems at their minimum entropy production rate are often said to be at steady state.

The classical approach to a thermodynamic analyses is to take the quasi-static approach. During a quasi-static process, the system is at all times infinitesimally near a state of thermodynamic equilibrium and all states through which the system passes can be described by means of thermodynamic coordinates referring to the system as a whole. An equation of state is valid for all these states. Zemansky and Dittman (1997) provide several examples.

The equation of states and relevant thermodynamic coordinates are understood for many nonliving systems. We are groping for this understanding with living systems. The equation of state notion for living systems is further discussed under a separate heading.

The quasi-static processes is an idealization that is applicable to all thermodynamic systems that can never be satisfied rigorously in the laboratory but can be approached with almost any degree of accuracy with nonliving systems. The applicability of the quasi-static approach to the study of the living system is debatable, as has been alluded to earlier.

The far-from-equilibrium notion has been characterized by 1) failure in the linear phenomenological laws (e.g., Fourier's, Stoke's, Fick's, Ohm's, etc.) to transport respective constituents; and, 2) the development of self-organized structures for energy dissipation. The 5/3ds law in turbulent dissipation (Tennekes and Lumley, 1972) is one example of such a consistent self organizing structure. Prigogine and Stengers (1984) discuss the notion of self-organizing structures. They propose that irreversibility is a source of order. Attractors as defined in chaos theory (Gleick, 1987) become the topographical "posts" around which mathematical descriptions may be defined. Wolfram (2002) further developed these ideas. The fact that these ideas have found some success in describing ecological systems has given currency to the notion that ecological systems are far-from-equilibrium. The robustness or usefulness of these descriptions to describe a similar system in another location is a current issue. The laws of transport still are generally applicable in many ecological systems. The choice of nearness or farness from equilibrium as an optimal approach for ecological system description is not yet firm.

Thermodynamic equilibrium cannot be assessed without identifying a goal function. The accepted goal function in the classical sense is the minimization of specific dissipation, originally proposed by Prigogine and coworkers (de Groot and Mazur, 1984). This concept is generally accepted to be the choice for describing a process not too far from equilibrium. This goal function is encapsulated in the notion that the Gibbs function $G=U+PV-TS$ will approach a minimum when plotted as a function of relative constituent concentrations or thermodynamic coordinates. One could generalize this to include all energy modalities as was effectively done in examples given by Cengel and Bowles (2001).

When life-bearing entities are introduced, the nature of the goal is not as clear. Ulanowicz (2000) uses the notion of ascendancy as a goal function. Ascendancy is based on network analyses concepts coupled with an introduction of information theory via the coefficients of the flow matrix. He argues that the ascendancy goal function likewise suggests a maximum power approach initially and moves toward a minimum specific dissipation rate as the system matures. One is referred to Ulanowicz (2000) for the details.

Fath et al. (2001) compared and contrasted 10 different goal functions, including the maximum empower function mentioned above as well as the ascendancy function (Ulanowicz, 2000). Other functions included the maximization of power, storage,

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energy, dissipation, cycling, and residence time. The minimizing of the entropy to exergy ratio and specific dissipation was investigated. The investigation was conducted by writing all the functions in the notation of the Patten (1978) network analyses nomenclature and discovering many similarities. Fath et al. (2001) stated that all the goal functions implied the following:

Get as much as you can (maximize input and first passage flow), hold on to it for as long as you can (maximize retention time) and, if you must let it go, then try to get it back (maximize cycling).

They went on to say that the notion of minimizing specific dissipation is the most encompassing because it captures all three aspects of the maxim in that it is dependent on maximizing storage faster than maximizing dissipation, which is empirically observed. The Ulanowicz (2000) argument for ascendancy could also be construed to support this conclusion. The prevailing of the minimizing specific dissipation goal function, with its ties back to near-equilibrium thermodynamic concepts, supports the notion that approaches for analyzing the far-from-equilibrium problems may be very similar to those of near-equilibrium problems once the coordinates are identified.

The equilibrium state may contain two or more phase-constituent states in a physical system. If one generalizes the phase to contain, for example, degrees of protein folding in biological systems, equilibrium may cover multiple phases and states. Haynie (2002) discusses equilibrium of microbiological systems at length. The topological of the thermodynamic coordinate system is typically pictured as a simple concave line or surface, with the bottom point representing the equilibrium point. Haynie (2002) generalizes the topology to include multiple local minimum points. Activation energy from outside the system is required to propel a system out of a local minimum zone to search for another minimum point. The validity of classical thermodynamic approaches is not certain in these more complicated topologies.

True thermodynamic equilibrium is not achieved in any steady state condition, although it may be well approximated in many steady state flows. True thermodynamic equilibrium requires cessation of macroscopic motion. Chemical reactions must cease, no heat may be transferred and there must be no momentum. One may extend this to the condition that no charge be transferred. In most cases, some of these conditions may be relaxed with few adverse consequences to the solution of the problem at hand. The nearness or farness from the equilibrium state may or may not affect the problem analyses.

K. Is ecological engineering possible?

Understanding the thermodynamics of the biosphere is by nature a speculative undertaking. Jorgensen (2001) and Svierzhev (2001c) present speculative approaches for computing thermodynamic parameters. These approaches seem to deviate from classical thermodynamics with the seemingly high levels of probability and speculation. However,

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from the historical perspective, the application of statistical mechanics principles to a system of atoms and molecules far too numerous to visualize to arrive at thermodynamic conclusions was also quite speculative. Indeed, the history of thermodynamics has been filled with speculation (Truesdell, 1980). The test of statistical mechanics speculation was the realization that many experimentally verified results squared will with empirically observable results.

Observations in ecological systems are limited due to the extreme large magnitude of these systems. Likewise, the development of reproducible strategies for ecological engineering design in diverse locations is the test of ecological thermodynamic hypotheses.

L. Summary statements

This course considered the laws of thermodynamics in the classical sense and investigated some models showing how these laws describe solids and gases at the microscopic level in the context of isolated, closed and open systems. We addressed the difficulties of extrapolating from nanoscale to macro scale, critically evaluating the implications of the scale change as related to the laws. We evaluated the impact of departing from near-equilibrium conditions to far-from-equilibrium conditions.

The seminar set forth the following broad objectives:

*Appreciate the pervasive nature of the laws of thermodynamics and thus how these first principles may serve as a basis for interdisciplinary science/engineering research.

*Appreciate the potentials and pitfalls of 1) scale-ups and 2) departures from equilibrium on reasonable application of the laws of thermodynamics.

Thanks to the contributions of each class member and the regular presence of Drs. Bernie Patten and David Gattie, we reached these objectives in excellent form.

Briefly, we concluded that in order to build a rigorous basis for physically based design, ecological or otherwise, one must begin with energetics. The system must be clearly defined, thermodynamic coordinates must be identified, and an effective equation of state must be developed. Thermodynamic coordinates may include temperature, energy, constituents, and possibly ecological orientors. One may then analyze many systems to determine the relative robustness of the coordinate set. As trends begin to emerge, ecological engineering will be on its way to taking its place with other engineering disciplines.

The literature surveyed suggests that yes, we can apply thermodynamic principles to develop a quantitative basis for design. The seminar likewise revealed some insights for so doing. This energetics seminar has served well to identify many of the required bases for commencing this effort. We must now set our sights towards this task.

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