

## **2006-112: ECOLOGICAL THERMODYNAMICS AND THE POSSIBILITY OF NEW THERMODYNAMIC INDICATORS**

**Ernest Tollner, University of Georgia-Athens**

Dr. Tollner received his BS and MS at the University of Kentucky and his Doctorate from Auburn University. He has been researching and teaching in the natural resources engineering area for 25 years at the University of Georgia.

# Concepts for an Evolving Course in Ecological Thermodynamics

Ernest W. Tollner and Caner Kazanci

Can thermodynamic principles enable a qualitative basis for ecological engineering design? New insights into interdisciplinary engineering endeavors, from classical modeling to nano–macroscale extrapolation and critical evaluation, weigh heavily on the pervasive nature of thermodynamics in the physical world. ENGR 8980 at UGA provides the basis for this kind of interdisciplinary research in a seminar format, with periodic oral and written reports to educate classmates on student findings. Working in three sections over 15 weeks to appreciate the potential and problems of scale-ups and departures from equilibrium on reasonable application of the laws of thermodynamics.

The first offering of the course left us with the impression that classical approaches to applying entropy were less than satisfying, particularly when large temporal and geographic scales were involved. Statistical mechanics can be used to predict thermodynamic properties when homogeneity and near equilibrium conditions can be reasonably assumed. Living systems with all their complexities add layers of complications. The purpose of this paper is to explore an analogue of statistical thermodynamics on an ecological scale.

The presentation will explore success and other directions taken in this course based on a fall 2003 offering. The pedagogical approach has been a loosely structured seminar that seems appropriate. We will spend some time looking at relations for conserved (e.g., force, mass, momentum) and nonconserved parameters (e.g., money, entropy). We will explore the possibility of using various network environmental analyses outputs to explain nonconserved indicators to see what commonalities may be useful.

## Introduction

The 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 macroscale, 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.

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.

An underlying sense pervaded that basing our definition of thermodynamic principles on molecular and atomic behavior was insufficient to describe ecological problems. Additional approaches were required to enable scaling from the molecular to the ecological temporal and spatial levels. The fundamental definition of entropy is based on a statistical distribution of molecular and atomic states. Once the distributions become multimodal scale-up becomes problematic without some additional tools. The purpose of this presentation is to introduce an inquiry that may lead to new approaches for analyzing thermodynamics of ecosystems. The approach will be oriented around network environment analyses (Gattie et al., 2005) and will be augmented by an alternative analysis based on a Lagrangian approach.

## **Fundamental Laws and Approaches of General and Statistical 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.

Isolated system: A system where no mass or energy is exchanged across the system boundary.

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. Whalley (1992) summarizes our knowledge of classical entropy, macroscopically and microscopically, as follows:

\*A process occurring at constant entropy is known as an isentropic process. Since entropy change is defined as  $\int (dQ_{rev}/T) dt$ , an isentropic change is both reversible and adiabatic.

\*The entropy change of the universe (the system and the surroundings) is the criterion of reversibility.

\*Entropy always increases (for an irreversible process) or remains constant (for a reversible process), never decreases.

\*An entropy change for a process can be calculated for a reversible change. This is then the entropy change for any process between these initial and final states.

\*Heat transfer across finite temperature differences is a cause of irreversibility.

\*A number of equations representing the combined first and second laws of thermodynamics are very useful because they are valid for any substance and for any type of change.

\*Using these equations for the combined laws, a convenient derivation of the shaft work in a reversible, steady-flow process is available.

\*Equations for the entropy change in an ideal gas are derived. From these, the equation of an isentropic change can be derived.

\*A sudden, unresisted expansion of a gas is an irreversible process.

\*The gas molecules are in continuous motion, giving rise to surface pressure, and to transport phenomena such as viscosity and thermal conductivity.

\*The main results from the kinetic theory of gases are given: for the velocity distribution, the pressure, the flux of molecules at a surface, and the transport properties.

\*Internal energy arises from the different types of energy possessed by the molecules: kinetic energy of translation and rotation, and vibrational energy.

\*The principle of the equipartition of energy shows how the energy is shared between these various types of energy.

\*Equations for the internal energy can be interpreted in the form of specific heats: both at constant volume and constant pressure.

\*From the values of the two principal specific heats, their ratio  $\gamma$  can be calculated. The calculated values agree well with experimental values.

\*Entropy is related to the probability that a state will occur. Disorder is more likely to occur than an ordered system. Transition to a higher probability, more disordered state involves an increase in entropy.

Zemansky and Dittman (1997) provide a concise overview of statistical thermodynamics for gases and solids. They argue that the number of energy states possible for a set of particles far exceeds the number of particles in a gas. The thermodynamic number ( $\Omega$ ) of a particular macrostate is given by

$$\Omega = \frac{g_1^{N_1} g_2^{N_2}}{N_1! N_2!} \dots \quad (1)$$

where  $g_i$  represents the number of quantum states yielding energy  $\epsilon_i$  and  $N_i$  represents the number of particles at that energy. The thermodynamic number is identical to the number

of ways a sample of  $N_i$  particles can be drawn (with replacement) from a population when particles  $N_i$  are indistinguishable. Equation 1 states that the total thermodynamic number is the product of the numbers of the respective  $N_i$ . Zemansky and Dittman (1997) show that this leads to an exponential distribution relating numbers of particles to a given group of quantum states ( $g_i$ ) and energy ( $e_i$ ) given as:

$$N_i = \lambda g_i e^{-\beta e_i} \quad (2)$$

where  $\lambda$  and  $\beta$  are constants and other nomenclature is as defined above. Equation 2 is commonly known as the Boltzmann distribution. It should be noted that other formulations for the thermodynamic probability exist and lead to modified forms of the Boltzmann distribution. We will return to these ideas after laying some foundation for analyses at the ecological scale.

### **Network Environ Analyses**

Network environ analyses presents ecosystems as complex networks of flows of a conserved tracer (Gattie et al, 2005). Network environ analysis quantifies the direct and indirect effects between system compartments, gives insight on how compartment inputs can affect flow between seemingly disconnected compartments, and helps explain how compartment throughflow relates to total system throughflow. A steady-state approach is utilized, which assumes that time approaches infinity and the analytical concern is not so much on how the system got to steady state, but rather on the network relationships that are evident once it has reached steady state. In this case, steady state refers to the macroscopic scale where compartmental storages are constant. Microscopically, the system is dynamic as boundary flows and intercompartmental transfers maintain steady-state conditions. Analytical results indicate that compartments not evidently related by intercompartmental flows, contribute substantively to total system throughflow, a network property. Here, the effects of inputs on each compartment have quantitative interpretation and indicate how boundary inputs affect all compartments.

The analysis is limited in that it currently is applicable only to steady-state models, although it has been extended to the dynamic case in at least one instance (Hippe 1983). Moreover, it does not take into account the influence of ecosystem organization across hierarchical levels nor does it currently allow for simultaneous analysis of multiple tracers. As with many other analytical approaches to ecological networks, NEA is highly dependent upon model construction, particularly the boundaries at which the observer has chosen to limit the analysis and the compartments included within the boundary. This indicates that NEA could benefit significantly from an advanced treatment of modeling theory whereby boundary delineation and compartment identification incorporate as much information as possible about the system of interest. NEA is viewed as a limiting steady state case of a dynamic systems analyses.

### **A Lagrangian View of Network Environ Analyses**

A prototype ecology represented by the figure below was analyzed using network environ theory and a "particle" simulation approach. The network environ theory, based

on state space and input-output modeling approaches represents a classical Eulerian approach to solving the problem and can be easily applied to problems of many scales. The particle simulation approach represents a Lagrangian ride through the system and is inherently difficult to apply to problems beyond the most simple. The Lagrangian approach is also based on steady state approaches. It appears at first glance to be dynamic in that pulses or packets of energy or mass are sent through the system in a discreet fashion from some known starting state. The starting state is an arbitrary zero mass or energy state that is admittedly meaningless. The transition probabilities from one node to the next are indeed similar to those in the transport matrix from network environment analyses and are derived assuming steady state. One possible connection with a dynamic analysis is that one may see an output response with zero inputs; however further investigations are needed.

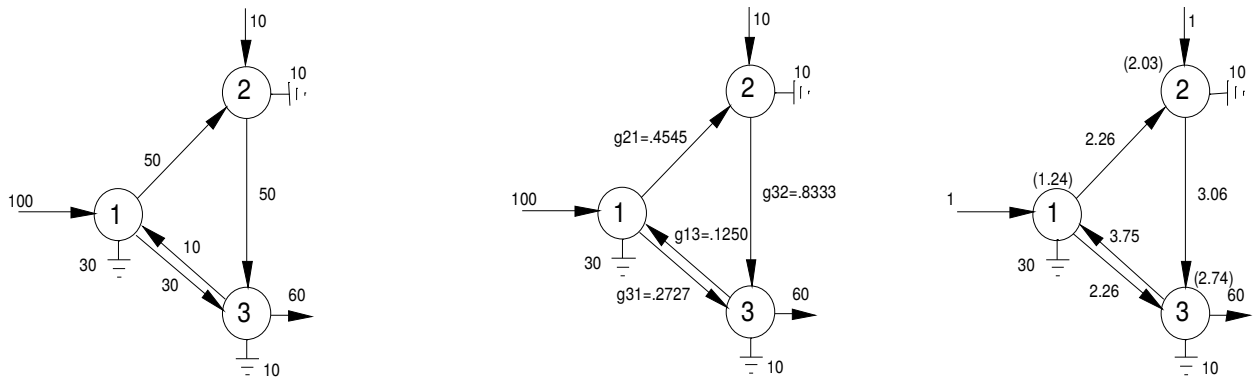
Nodes in the Lagrangian model receive inputs from other indicated nodes based on probabilities of total mass or energy at that node. For example, node 1 receives a total of 110 energy units in Figure 1. In the steady state condition, 50 of those units go to node 2, for a probability of 0.4525 as shown in Figure 1. One must compute the transport probabilities for each node as shown in Figure 1. An excel spreadsheet provides a suitable platform for a very simple implementation of the Lagrangian concept.

The basic challenge of the Lagrangian analysis is to track the route traveled by each packet of mass or energy. The analysis is straightforward unless the possibility of recycle exists, as is the case in Figure 1. Energy packets in Figure 1 represent 0.1 energy units. A group of 1000 packets were introduced into the network at node 1 and 100 were introduced into the network at node 2 for each pulse event. The direction of the packets to a given node depends on the probability of flow in a given direction. The probability is figured by dividing the flow in a given direction by the total outgoing flow from the respective nodes.

Energy packets enter the system at an arbitrarily defined state of "1". Passage through a node causes an incremental change of the state by 1. Therefore packets entering at node 1 have a state of "2" as they go to node 2 or node 3. Packets traveling the longest path would have a value of "4" as they returned to node 1. Due to the recycle between node 3 and node 1, multiple system snapshots are required to determine the distribution of states contained in the nodes. Each snapshot was made after passage of packets around the longest route back to node 1. After 4 snapshots, packets can have accumulated as many as 13 different state increments, with state number (e.g., history) becoming exponentially more complicated with each pulse event. The analysis was limited to 4 snapshots due to logistic considerations in using the excel platform. The probability of energy persisting in the network with a high state becomes very low. Knowledge of energy state persisting in the network may provide insights into network behavior, thus we desire to track energy state distributions.

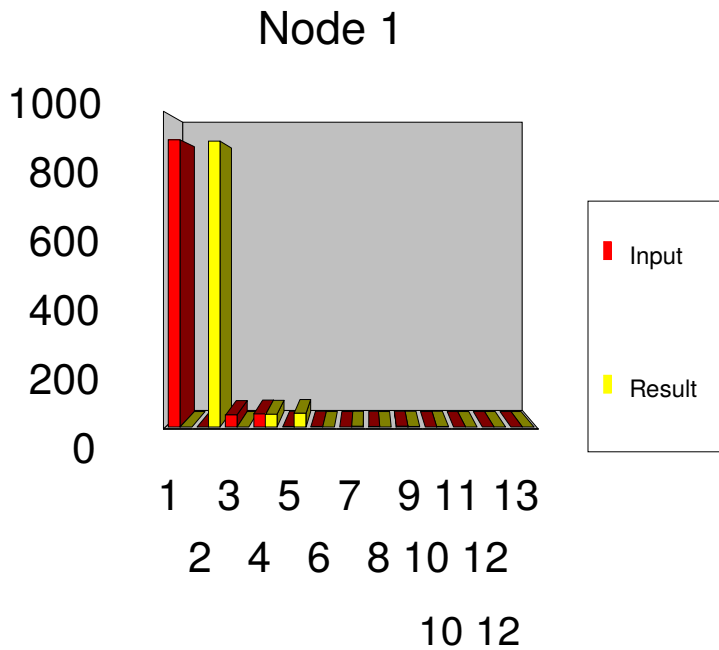
Some packets of energy at a given node may represent very low quality energy while most represent reasonably high quality energy. The assumption is that travel through the network degrades the quality of the energy. The low quality energy history

represents past history. A working hypothesis of this inquiry is that interesting possibilities may exist when one places very low quality energy along side of high quality energy. In a true steady state analysis, packets can accumulate very low energy levels, albeit the probability of observing these packets becomes extremely small as will be seen below.



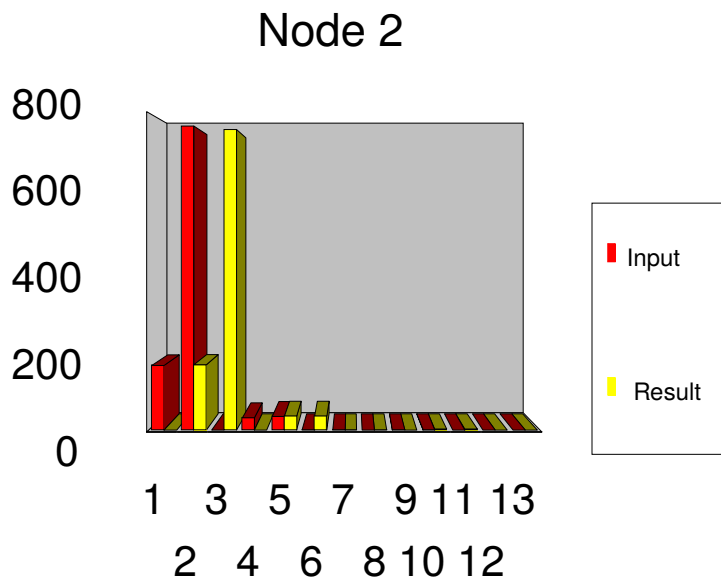
**Figure 1. Archetypical network environ showing energy flow through a simple 3-node system with two inputs, a recycle loop, dissipation and an output.**

Energy qualities of the nodes of Figure 1 are shown in Figures 2, 3, and 4, respectively assuming 4 pulse events. The fact that some packets at node 1 are not 1000 is due to the recycle from node 3. Similar explanations exist for the other nodes.

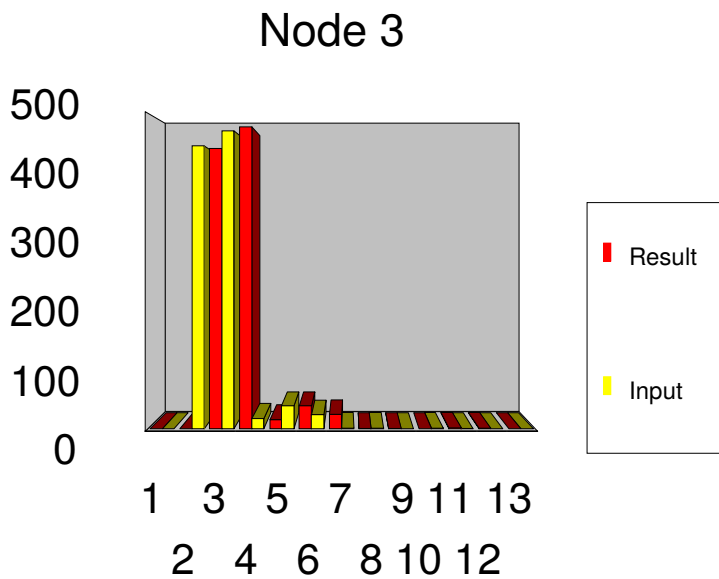


**Figure 2. Histogram showing hypothetical states of energy packets residing in Node 1 after 4 pulses, based on an average over 10 runs.**





**Figure 3.** Histogram showing hypothetical states of energy packets residing in Node 2 after 4 pulses, based on an average over 10 runs.



**Figure 4.** Histogram showing hypothetical states of energy packets residing in Node 3 after 4 pulses, based on an average over 10 runs.

Details of history at node 1 are shown in Figure 5. The Shannon information entropy is shown along with the Boltzmann entropy (where the Boltzmann constant is arbitrarily assigned as 1). The mixing of packets with different energy states and resulting effects of 'far from equilibrium' conditions (De Groot and Mazur, 1984) occur is of interest from a thermodynamic viewpoint. Each network will have different properties due to its inputs, outputs, elements, and element connections.

Input to Node 1			Output from Node 1					
State	Mean	SD	Shannon Entropy	Bolt. Entropy	Mean	SD	Shannon Entropy	Bolt. Entropy
1	912.6	9.08	-0.1204	0.0915	0	0.00	0.0000	0.0000
2	0	0.00	0.0000	0.0000	908.1	8.79	-0.1263	0.0964
3	39	7.53	-0.1825	3.2442	0	0.00	0.0000	0.0000
4	41.6	4.77	-0.1908	3.1797	40.4	3.89	-0.1870	3.2089
5	1.1	1.10	-0.0108	6.8124	43.3	8.84	-0.1961	3.1396
6	2	1.56	-0.0179	6.2146	1	1.25	-0.0100	6.9078
7	0.1	0.32	-0.0013	9.2103	2.8	1.48	-0.0237	5.8781
8	1.2	1.23	-0.0116	6.7254	0.2	0.42	-0.0025	8.5172
9	2.4	1.71	-0.0209	6.0323	2	1.70	-0.0179	6.2146
10	0	0.00	0.0000	0.0000	2	1.56	-0.0179	6.2146
11	0	0.00	0.0000	0.0000	0.2	0.42	-0.0025	8.5172
12	0	0.00	0.0000	0.0000	0	0.00	0.0000	0.0000
13	0	0.00	0.0000	0.0000	0	0.00	0.0000	0.0000
	1000		0.5564	41.5104	1000		0.5839	48.6944

**Figure 5. Example histograms showing details of contacts of packets entering and leaving Node 1 after 4 pulses.**

Another aspect of the Lagrangian analysis is to consider what the number of nodal contacts that the energy packets in a given node have completed. Each packet of energy by definition contacts a packet one time in the process of entering and leaving a node. This simple approach does not introduce the storage concept, which may result in multiple contacts between entrance and exit. Results are summarized in Table 1. The input contact average at node 1 is notably higher than 1 due to the recycle with node 3. As one proceeds to node 2, the contact is nearly two because the impact of recycle with node 3 is greatly diminished. Node 3 is complicated by the input from 1 and 2. The most interesting note that the effective change of each node is slightly higher than a simple contact.

Is all energy equal in the potential work it can accomplish? It is assumed herein that each time an energy bundle passes through a node, it accumulates states (e.g., history) related to the number of nodes it has passed while within the system. The total energy within a system may therefore contain a diverse history. The heart of the Lagrangian analysis is to develop that history for each node in the system. Having this history enables one to compute a measure of homogeneity of the energy known as the Shannon information entropy in a classical sense. It was interesting to compute the Shannon information entropy analogue for the inputs and outputs of each node based on distributions of the respective conditions similar to those shown in Figure 5. The Shannon information entropy ( $S_{\text{Inform}}$ ) and Boltzmann entropy ( $S_{\text{Boltz}}$ ) are respectively computed using the following equations:

$$S_{\text{Inform}} = -k_B \sum_{\text{State}=1}^{\text{No.States}} p_i \log_2 p_i$$

where  $p_i = \text{node}_i / \sum_{\text{State}=1}^{\text{No.States}} \text{node}_i$

$$S_{\text{Boltz}} = \sum_{\text{State}=1}^{\text{No.States}} k_B \text{Ln} (1/p_i) \tag{3}$$

Note that  $\log_2 p_i$  and  $\text{Ln} \frac{1}{p_i}$  were forced to zero if  $p_i = 0$ .

Shannon and Boltzmann entropy values at the entrance and exit of each bin are shown in Table 1. Details of the entropy calculations for Node 1 are also shown in Figure 5. Nodes 1 and 2 showed an increase in information entropy and a decrease in Boltzmann entropy. Node 3 exhibited the opposite behavior, due to the recycle with node 1. Node 3 was moving in a different direction relative to equilibrium than were nodes 1 and 2. Jorgensen and Svirezhev (2004) seem to rely on the Shannon entropy more so than the Boltzmann entropy. The dissipative effects coupled with the accumulation of capacity to do work is consistent with Prigogine's assertion (see Prigogine and Stengers, 1984) that thermodynamic systems, while dissipating much energy, may have small zones moving further from equilibrium. A more exhaustive analysis of this system and additional systems may provide additional insights as to which definition of entropy is the best for ecological systems.

Table 1. Summary of Nodal Inputs and Actions

Node	Input Contact Average	Output Result Average	Effective Change	S <sub>inform</sub>	S <sub>Boltz</sub> <sup>1</sup>	Entropy Trends	
						S <sub>inform</sub>	S <sub>Boltz</sub>
1	1.25		1.01	0.556	41.51	+	+
		2.26		0.585	48.69		
2	2.03		1.03	1.093	44.81	+	-
		3.06		1.143	43.28		
3	3.75		1.01	1.467	58.38	-	+
		2.74		1.455	64.70		

<sup>1</sup>An arbitrary value of 1.0 is assigned to the Boltzmann constant.

It is interesting to explore some parallels between the classical statistical thermodynamics definition of thermodynamic probability as shown in Equation 1 and the ecological thermodynamic probability leading to the distributions in Figures 2 through 4. In classical thermodynamics,  $g_i$  represents the number of possible quantum state combinations leading to a given energy level  $e_i$ . One possible ecological parallel to  $g_i$  is the number of possible contact combinations leading to a given energy level  $e_i$ . In

classical thermodynamics,  $N_i$  represents the number of atoms/molecules having energy level  $e_i$ . The ecological parallel is the number of energy packets having energy level  $e_i$ . The energy packet thus becomes the basic quanta of energy in this analysis. Further theoretical work may enable one to relate the ecological quantum to the classical quantum.

A fundamental premise of network environmental analyses is that the system is at steady state. Considering the Lagrangian analyses, the nature of steady state becomes interesting. A system can have equal inputs and outputs from the Eulerian viewpoint but still be changing its configuration.

According to Reynolds (1968), the Shannon information entropy is equivalent to the Gibbs definition of entropy (where we have taken the Boltzmann constant equal to unity). The Boltzmann distribution assumes that quantum states are equally possible in the universe of  $\Omega$  numbers of quantum states. The Gibbs (or Shannon information) formulation does not impose this restriction. It is felt that the Shannon formulation may be more appropriate at this juncture. Resolving the apparent discrepancy between the Shannon and Boltzmann entropy trends would be aided by a similar analysis of additional models.

### **Is Ecological Thermodynamics Possible?**

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. The above statements imply that organisms are on a trajectory leading to death.

A central question of this enquiry is: Can we use an expanded definition of entropy to discern how an ecosystem will organize itself? With nonliving systems, the system goal functions (e.g., open systems  $\rightarrow$  minimum entropy production; closed systems  $\rightarrow$  maximum entropy) are now well understood. When life is introduced, the nature of the goal function is a subject of study (see Fath et al 2004). They tested several hypotheses involving thermodynamic description of the orientation or natural tendency that ecosystems follow during succession. Specifically, five thermodynamic orientors were tested: minimize specific entropy production, maximize dissipation, and maximize exergy storage (includes biomass and information), maximize energy throughflow, and maximize retention time. These thermodynamic orientors are known to be present to some degree during succession, and here we present a refinement by observing them during different stages of succession. They view ecosystem succession as a series of four growth and development stages: boundary, structural, network, and informational. They demonstrate how each of these ecological thermodynamic orientors behaves during the different growth and development stages, and show that while all apply during some stages only maximizing energy throughflow and maximizing exergy storage are applicable during all four stages. It was concluded that the movement away from thermodynamic equilibrium, and the subsequent increase in organization during

ecosystem growth and development, is a result of system components and configurations that maximize the flux of useful energy and the amount of stored energy.

It is felt that one can link classical thermodynamics and ecological scale thermodynamics by probabilistic approaches based on Lagrangian interpretations of network environmental analyses. As a step in this direction, one could consider the exergy of each input, perform the Lagrangian analyses for many pulse events, and then treat each energy history as a separate energy state. One could allow the quality of the incoming energy to vary. Thermodynamic properties could be computed for each node using the weighting based on numbers of packets at particular states. A model such as Arena (see Kelton et al 2004), which is a discrete model enabling one to track attributes of individual packets, would aid in tracking the state of more complex systems.

A careful look at how cycling occurs in ecological systems and associating the cycling with the blending of mass and/or energy of varying states may offer many insights into ecological behavior. It is believed that systems offering highly diverse energy and mass will likely be much more robust than those with simplified dynamics. Much work remains to be done as we identify appropriate indicators. Jorgensen (2001, 2004) and coworkers and Patton (1978) and coworkers (e.g., see Fath et al 2004) provide much insight into this problem and potential solutions.

Can we gain insight into how one may relate these findings to a definition of ecological entropy? What are the ecological counterparts to the summary statements developed by Whalley (1992)? Can we use this formulation of entropy to determine how systems may develop? Understanding the thermodynamics of the biosphere is by nature a speculative undertaking. Jorgensen (2001) and Jorgensen and Svirezhev (2005) present speculative approaches for computing thermodynamic parameters. However, 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 with empirically observable results.

The approach needs evaluation on many other systems. Students will be asked to tackle other simple network configurations. Due to the similarities of the Lagrangian and classical view of network analyses, it is believed that aspects of network analysis can be used to derive the Shannon entropy values. Further work is needed on how to more closely couple the Boltzmann entropy on the molecular scale with the contact properties of nodes in an ecological network. What are the corresponding ecological thermodynamic properties paralleling the above list of classical thermodynamic properties? These and related questions must await future inquiry and will form the basis of discussions in future offerings of the ecological energetics course.

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