ESCI 341 – Atmospheric Thermodynamics
Lesson 10 – The Physical Meaning of Entropy

References: *An Introduction to Statistical Thermodynamics*, T.L. Hill
An Introduction to Thermodynamics and Thermostatistics, H.B. Callen
An Introduction to Information Theory: Symbols, Signals and Noise, J.R. Pierce

STATISTICAL MECHANICS

- **Unlike other thermodynamic variables (e.g. *U, T*, *H*, *G*, *F*), entropy seemingly lacks a physical meaning.**
- **Entropy does have a concrete physical meaning, but its meaning is found via the field of *statistical mechanics*.**
  - **Statistical mechanics is also referred to at times as *statistical physics*, *thermostatistics*, or *statistical thermodynamics*.**
- **Thermodynamics applies to *macroscopic* (large) systems consisting of on the order of at least 10^{20} molecules.**
  - **Thermodynamics looks at the large scale properties.**
- **Statistical mechanics looks at the molecular level.**
- **Statistical mechanics and thermodynamics are intimately related.**
  - **Thermodynamic concepts such as pressure and temperature are tied to processes occurring on the molecular level, but averaged over a large number of molecules.**
- **Air parcels, cloud droplets, etc. are all macroscopic systems, and so as meteorologists we get along just fine using thermodynamics. However, in order to really understand entropy we have to resort to statistical mechanics.**
- **This lesson is just a very, very brief overview of the field of statistical mechanics, and is meant only to give a flavor of how it relates to thermodynamics. In particular, the main objective of this lesson is to give a better understanding of entropy.**

QUANTUM STATES

- **A system of matter exists in discrete quantum states.**
- **Each *quantum state i* has a certain *energy* E_i associated with it.**
- **For macroscopic objects the difference in energy between adjacent energy levels is infinitesimally small.**

- For macroscopic systems we don't need to bother with quantum states, as it appears that there is a continuous spectrum of energy.

- **For microscopic systems the energy spectrum is not continuous, but is discrete.**

QUANTUM FLUCTUATIONS

- **Systems do not remain in a single quantum state, but *actually fluctuate through all available quantum states*.**
  - ***Over a long period of time the system will actually spend some finite amount of time in every available quantum state*.**
- **The energy of our microscopic system will therefore fluctuate as it moves from one quantum state to another.**
- **The probability of finding the system in a specific quantum state *i* depends on the energy of the quantum state, and the temperature.**
- **The probability is given by**

$$P_i = \frac{e^{-E_i/kT}}{Q}, \qquad \textbf{(1)}$$

where the function *Q* is called the *partition function* and is given by

$$Q = \sum_i e^{-E_i/kT} \qquad \textbf{(2)}$$

(*k* is the Boltzmann constant).

PHYSICAL MEANING OF ENTROPY

- **We've very briefly attempted to describe the relationship between thermodynamics and statistical mechanics. The main reason we've done this is so that we can try to give entropy a physical meaning.**
- **In statistical mechanics entropy is given by**

$$S = -k \sum_i P_i \ln P_i \qquad \textbf{(3)}$$

where P_i is the probability of the system being in quantum state *i*, given by Eqn. (1).

- **Some examples may help. Imagine that a hypothetical system has three different possible quantum states, *i* = 1 to 3, with probabilities given by**

$$P_1 = 11/16$$
$$P_2 = 3/16$$
$$P_3 = 1/8$$

then from equation (1) the entropy equal to

$$S = -k\left[(11/16)\ln(11/16) + (3/16)\ln(3/16) + (1/8)\ln(1/8)\right] = 0.831k.$$

- **If instead all three quantum states had the same energy level, and were therefore all equally probable, the entropy would be**

$$S = -k\left[(1/3)\ln(1/3) + (1/3)\ln(1/3) + (1/3)\ln(1/3)\right] = 1.099k.$$

  - **The second system has higher entropy because there is less certainty as to which quantum state the system is in.**
- ***Entropy is a measure of the uncertainty of the quantum state of the system*.**

ENTROPY, TEMPERATURE, AND ABSOLUTE ZERO

- **At higher temperatures the probabilities of the system occupying a higher-energy quantum state become larger.**
  - **The probabilities are spread over more possible quantum states.**
  - **This leads to more uncertainty as to the quantum state of the system, and is why higher temperatures generally have higher entropy.**
- **As a system is cooled, the lower-energy quantum states have the highest probability, and the higher-energy quantum states become less probable.**
  - **There is more certainty of the quantum states at low temperature, and is why lower temperatures are associated with lower entropy.**
- **As absolute zero is approached, the only quantum states available are those that have the minimum amount of energy. The higher-energy quantum states are so improbable that it is nearly certain which states the system are in, and the entropy approaches zero.**
- **If the lowest energy state is nondegenerate, then at absolute zero the system is certainly in this single quantum state.**
  - **From equation (3) the entropy would be zero at absolute zero for a system having a nondegenerate, lowest energy quantum state.**

- **If the system has a degenerate lowest-energy level (multiple quantum states having the lowest possible energy), then the entropy of the system will be nonzero even at absolute zero.**

ENTROPY, UNCERTAINTY, AND RANDOMNESS

- **Because entropy is associated with the amount of uncertainty of the quantum states of a system, higher entropy is often associated with randomness (high uncertainty) while lower entropy is associated with order (low uncertainty).**
- ***It is important to keep in mind that entropy was defined in terms of quantum states* in the context of statistical mechanics and thermodynamics.**
- **The concept of entropy can also be applied in other contexts.**
  - **For example, imagine a bin containing both red beads and white beads. If the red and white beads are separated, they presumably have more order. If they are mixed together, then presumably they are more disordered. Some would say that the mixed beads have a higher entropy than the separated beads. Is this the same as thermodynamic entropy?**
- **The type of entropy that is applicable to the bead example appears in a branch of mathematics known as information theory (see the Pierce reference for a good, layman's description of information theory).**
  - **Thermodynamic entropy and information theory entropy are analogous, and behave in similar ways.**
  - **When people speak of randomness in nature as having higher entropy than order in nature, it is the entropy from information theory that they speak of.**
  - **I am not an expert in information theory, but I have had experts in this field attempt to convince me that the two concepts are the same, and that there is only one form of entropy that applies to both. I am not certain of the answer.**

A FINAL THOUGHT ON THE PARTITION FUNCTION

- **The partition function is of fundamental importance when relating statistical mechanics to thermodynamics, because all macroscopic state variables can be found from the partition function.**
- **For example:**

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$U = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$$

$$S = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} + k\ln Q$$