Thermodynamics 101

Presentation given in the course of the Master’s Programme *Environmental Management* – Module 2.1.1 “Ecosystem Analysis” –

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Preface

Thermodynamics is a terrible game:

0. You have to play.
1. You cannot win.
2. You cannot break even—except on a very cold day.
3. It does not get that cold.
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Introduction
What’s it all about?

There are two different approaches to thermodynamics:

Classical Thermodynamics is the branch of physics concerned with the conversion of different forms of energy.

Statistical thermodynamics is the branch of physics that describes the thermodynamic behavior of macroscopic systems on basis of the properties of their molecular constituents.
Introduction

Classical Thermodynamics: How does it work?

As a phenomenological theory, it deals with

- macroscopic objects (which contain a large number of particles) and their
- macroscopic properties (state variables like mass, volume, pressure, temperature, energy, entropy, and enthalpy)
- that can be observed and measured in experiments
- from which one can abstract and set up axioms based on the empirical findings (phenomenology).
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Classical Thermodynamics: What is it good for?

At its origins, during the Industrial Revolution, thermodynamics was concerned with (steam) engines and their efficiency.
Introduction

Classical Thermodynamics: Its Fathers

Sadi Carnot’s *Reflections on the Motive Power of Fire* (1824) analyse the efficiency of steam engines and mark the start of thermodynamics as a modern science.

William Thomson (1st Baron Kelvin aka Lord Kelvin) invents the absolute temperature scale in 1848 and coins the term “thermodynamics” in 1849.

Rudolf Clausius’ *Über die bewegende Kraft der Wärme* (1850) serves as a milestone of thermodynamics. Clausius specifies the second law idea of Carnot and later, in 1865, introduces the macroscopic concept of entropy.
Introduction
Classical Thermodynamics: What Are Its Limits?

Problems with classical thermodynamics:

► Many questions remain open:
  ► Why do all gases behave similarly?
  ► Can temperature be negative?
  ► What is this entropy thing, by the way?

► All constants and parameters have to be derived from experiments. We have no clue about their possible values.

► It provides no information about the states or even the existence of molecules.

► It has only weak if any predictive power: We can build a refrigerator, but we cannot design a proper cooling fluid for it—we can only choose from those we know.
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Statistical Thermodynamics in a Nutshell

The statistical approach is a first principle theory that

▶ derives macroscopic properties (state variables and functions)
▶ from the constituent particles and the interactions between them
▶ by connecting thermodynamic functions to atomistic phenomena (including quantum mechanics).

It thus

▶ gives thermodynamics a molecular interpretation and
▶ serves as a bridge between macroscopic and microscopic system properties.
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James Clerk Maxwell describes the velocity distribution of molecules in 1860, laying the foundation for what is nowadays known as “Maxwell-Boltzmann kinetic theory of gases”.

In 1877, Ludwig Boltzmann shows the logarithmic connection between entropy and probability—which is still the best definition of entropy we have.
The Fundamental Laws of Thermodynamics

Preliminary Remark

Classical thermodynamics is, like plane geometry, based on axioms and postulates. Only, in thermodynamics these are called laws.
The Fundamental Laws of Thermodynamics

Zeroth Law: Thermodynamic Equilibrium

*When two systems are each in thermal equilibrium with a third, they are in thermal equilibrium with each other.*

▶ “Thermal equilibrium” means: The temperature gradient between the two systems is zero, i.e. both systems are at the same temperature.
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The Fundamental Laws of Thermodynamics

First Law: Conservation of Energy

Energy (and hence matter) can neither be created nor destroyed.

- Energy can be transferred from one system to another.
- Energy can be transformed from one manifestation into another: chemical, mechanical, thermal, electrical, gravitational potential energy etc.
- The internal energy of an isolated system is constant: \( dU = 0 \).
- The internal energy of a closed system can only be changed through heat transfer or work: \( dU = \delta q + \delta w \).
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Second Law: Increase of Entropy

The total entropy change (system + surroundings) is always greater than or equal to zero for any change of state of the system: \( \Delta S \geq 0 \).

- The entropy of an isolated system never decreases.
- Heat does not spontaneously flow from colder into warmer systems (but always in the opposite direction).
- Energy of all types spontaneously flows from being localised or concentrated to becoming more dispersed or spread out, if it is not hindered.
- There are as many variations of the second law as there are thermodynamicists.
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What Is Entropy Anyway?

Classically, entropy measures the spontaneous dispersal of energy: how much energy is spread out in a process (and cannot be used to do thermodynamic work), or how widely spread out it becomes—at a specific temperature: \( dS \geq \frac{\delta q}{T} \).

Statistically, it measures the amount of uncertainty that would remain about the exact microscopic state of the system, given a description of its macroscopic properties: 
\[
S = -k \sum_i P_i \ln(P_i), \text{ where } k \text{ is the Boltzmann constant and } P_i \text{ the probability of the } i^{th} \text{ microstate to be occupied}.
\]

- Entropy is not disorder or a measure thereof. Rearranging objects does not change their entropy.
- Classical entropy is always connected with energy in general, and specifically with energy that is being or has been dispersed.
- Statistical entropy is not defined in terms of energy (nor vice versa), but in terms of probability spread out in state-space.
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Third Law: Zero Temperature

*Absolute zero cannot be reached by any procedure in a finite number of steps.*

- All processes cease as temperature approaches zero.
- As temperature approaches zero, so does the entropy.
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Ecosystem Relevance

Why Bother?

Based on the macroscopic flow of energy (and matter), thermodynamics is considered to be well suited to describe ecosystems from an holistic point of view.

Ecosystem Thermodynamics will be the subject of the second part of this presentation, to be given on 2006-07-05.
“Thermodynamics is a funny subject. The first time you go through it, you don’t understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don’t understand it, but by that time you are so used to it, it doesn’t bother you any more.”
Ascribed to Arnold Sommerfeld (German physicist and teacher, 1868–1951)

Thank you for your attention!
References
For Further Reading . . .


