3.23 Lecture 1

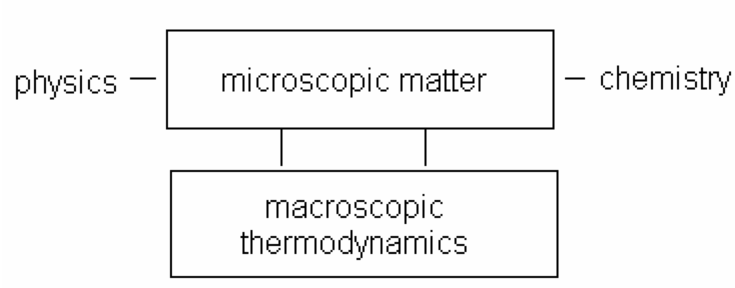
What is thermodynamics?

Thermodynamics involves the flow of energy. It is a macroscopic framework of energy flows and how they affect the properties of a system. The description of how energy flows affect the properties of a system is a consequence of the macroscopic framework.

Energy is the coordinate in thermodynamics. The derivatives of energy are forces are forces and displacements.

Thermodynamics never generates data but rather describes relations. The equation $pV = nRT$ is not thermodynamics; it is an input into thermodynamics.

Thermodynamics deals with macroscopic variables or averages. Minimize over them, integrate, or average to make variables disappear.



The link between microscopic matter and macroscopic thermodynamics is statistical mechanics, which is a theory of averaging. This is used to obtain macroscopic properties.

There is no physics or assumptions in thermodynamics. It is extremely powerful and not limited. In two laws of thermodynamics there are no assumptions about macroscopic laws.

How does this fit in with other disciplines?

Mechanics	Newton	mass, velocity, force, acceleration	1643 – 1727
Elasticity	Hooke	stress, strain, elastic constants	1635 – 1703
Electromagnetism	Maxwell	electric field, polarization, mag.	1831 – 1879
Thermal	Fourier	heat flows down a temp. gradient	1768 – 1830

Mechanics and thermodynamics united with the theory of the steam engine. This started with Newcomen (1663 – 1720) and Watt (1736 – 1819). Lord Kelvin primarily united mechanics and thermodynamics. Hemholtz and Clausius integrated thermo with electromagnetism.

A common connection is energy. By putting all on a same scale, fields were integrated. Thermodynamics is properly named. People wanted to make engines, and there was a unification of the field of thermo and mechanics.

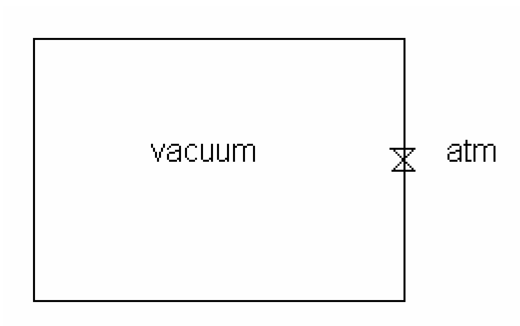
There is a need to develop constitutive equations for each field. There is a need to know, for instance, that the stress is equal to the strain times Young's modulus. The equations of state make thermodynamics complete.

Reading

The material in Zemonsky in Chapters 1 – 4 covers this and the next lecture.

What is a system?

A system is a collection of matter we want to study. It is specified through some rules and does not need to be coherent; it can be abstract. Consider the following system of a tank and valve.



Gas enters the tanks. What is the temperature when the system reaches equilibrium? Define the system to be the gas that will be in the tank.

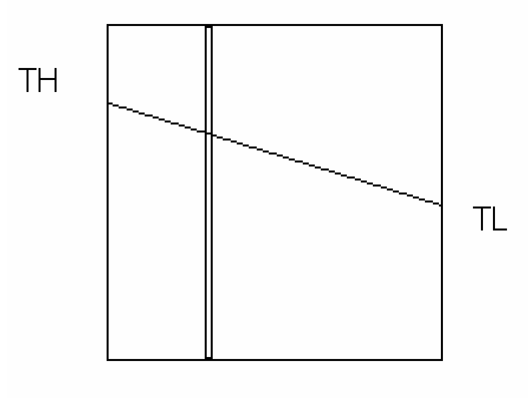
The oversight of a drop in temperature is a classic source of experimental error. There was a report in Science that nanotubes could store 30 – 40 % hydrogen by weight. There was an assumption that the temperature of the gas stayed constant.

Universe, Environment, and System

Everything that is not in the system is the environment.

$$Environment = Universe - System$$

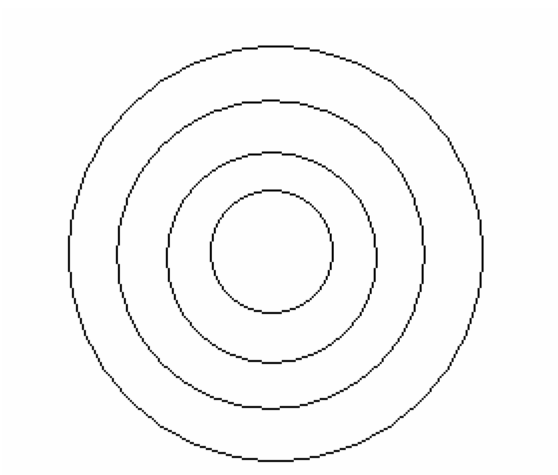
Systems do not need to be homogeneous. Thermodynamics can be applied to non-equilibrium situations.



Integrate homogeneous sections to get thermodynamic properties

$$S_{total} = Integrate[S(T), T_C, T_H]$$

This same method can be applied to situations with concentration gradients. Integrate in bands.



This is how Fick's law was developed. The maximizing of entropy leads to Fick's law.

This methodology does break down. It's not possible to do thermo with one atom.

When it is possible to integrate on a particular length scale, it may be necessary to introduce a new surface and give it special properties (surface energy, entropy)

Boundaries of systems

Permeable	open systems
Impermeable	closed systems
Adiabatic	no heat flow
Diathermal	heat flow
Rigid	
Deformable	

A distinction of variables

Extensive	scale with system size (*N, U, …)*
Intensive	do not scale with system size (*T, P, …)*

Normalizing variables

Extensive variables are normalizable and when normalized play the role of extensive variables

$$V / N \rightarrow \text{specific volume} = \underline{V}$$

The volume when normalized by some quantity is written $\underline{V}$. The term can be thought of as a density. Strain is an elongation density

$$dl / l = \varepsilon$$

Bundaries

Think of boundaries as constraints on extensive variables. The following boundaries restrict associated extensive variables

Permeable	Mole Number
Adiabatic	Entropy
Rigid	Length

State variables of a system

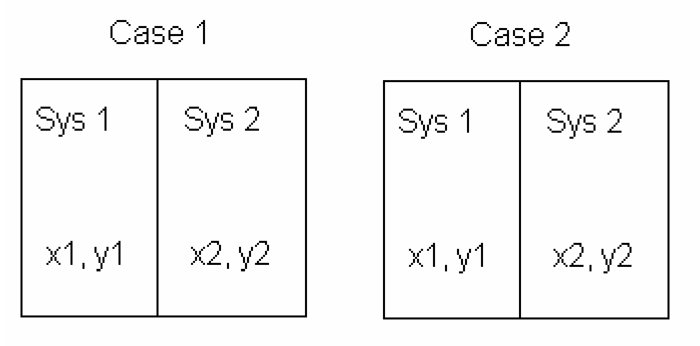
These are variables that describe the macroscopic state. Examples are below

T, P, V, N, shape, color, dislocation density

These are macroscopic observables. Some of them are known from a subset of variables

Concept of temperature

A proof of the existence of temperature is based on observation.



Find the relation between variables based on different boundaries. With an adiabatic boundary, all variables can be set independently. With a diathermal boundary, the following relation holds

$$F(x_1, y_1, x_2, y_2) = 0$$

A constant that appears is temperature. This lies in the 0^{th} law.

Zeroth law

If A and B are in thermal equilibrium and B and C are in thermal equilibrium, then A and B are in thermal equilibrium.

$$F^{AC}(X_A, Y_A, X_C, Y_C) = 0 = F^{BC}(X_B, Y_B, X_C, Y_C)$$

Eliminate Y_C from the equality

$$Y_C = f^{AC}(X_A, Y_B, X_C) = f^{BC}(X_B, Y_B, X_C)$$

There are no assumptions about X_C. There is some function such that

$$\partial^A(X_A, Y_A) = \partial^A(X_B, Y_B) = \partial$$

There is a property in system A that is a function of variables in system A and this property is equal to a property in system B. This is defined as temperature.

This can be a generalized proof to any intensive variable where the system is separated by a diathermal wall. When the extensive variable is not restricted by the boundary, the intensive variable will be equal. The conjugate intensive has to be the same between two systems. When there is a movable boundary, the pressure must be the same. Variables come in conjugate pairs, and the derivative of one with respect to another makes units of energy.

How to define ∂ is a matter of convention. The temperature is related to the height of the column of mercury with a scaling factor when using a thermometer. Defining ∂ is a matter of scaling units. Temperature could be expressed in terms of volts.