1. Introduction (Chapters 1 and 2)

Goal: Review the empirical laws of TD so that we can contrast them with the more fundamental approach in SM

In thermodynamics (TD) one attempts to understand the properties of macroscopic objects such as a liter of gas , a wafer of Si, melting block of ice etc. One begins with a set of laws or axioms from which one derives relationships between *macroscopic* variables of the system using empirical information. There are basically two kinds of observables-- *intensive* and *extensive* quantities. Intensive quantities, such as temperature, pressure p and density ρ are independent of the system size. Extensive quantities such as mass M, internal energy U, volume V , magnetization M, and entropy scale with the system size. In TD there is no need to know anything about *microscopic degrees of freedom.* In fact TD was developed in the 1800's at a time when scientists did not believe in atoms or molecules.

In contrast in statistical mechanics (SM) we typically begin with knowledge of the microscopic constituents (and possibly their interactions) and apply the laws of physics and statistics to derive macroscopic quantities and relationships between them, with minimal empirical information.

Thermodynamics	Statistical Mechanics
Establishes relationships between macroscopic variables using empirical information	Macroscopic quantities are calculated from assumptions about microscopic constituents (atoms and molecules)
4 basic laws or axioms	A single hypothesis- all microstates are equally likely (Ergodic Hypothesis or EH) along with the laws of physics e.g. quantum mechanics.
0 th law : If systems A and B are in equilibrium with C then A is in equilibrium with B.	Follows from the EH.
1rst law: heat and work are equivalent and energy is conserved,	Energy is conserved.
2nd law: Entropy in an isolated system can only increase. Changes in entropy are well defined . However the meaning is a bit vague and temperature is not well defined.	An isolated system tends to it most probable state. Follows from the EH. Entropy and temperature are well defined quantities.
3rd law: At absolute zero (T=0) the entropy approaches a constant value.	At T=0 the system in its the ground state and entropy is zero. There are exceptions to this "law" such that the entropy is non zero at T=0.
Only average quantities are calculated.	Fluctuations can also be calculated. Especially important in small systems or near phase transitions.

Empirically based. Experimental data is the main input. Widely applicable.	Minimal experimental data needed but relatively few systems can be treated.
Quantum mechanics is not relevant.	Quantum mechanics naturally fits in. In a sense it is needed for self consistency.

Empirical Temperature θ and absolute temperature T

Consider a system A which is isolated from its surroundings. It is in *thermal equilibrium* if no observable changes occur. Of course this is an idealization since no system is truly isolated and time independent. The universe and everything in it is constantly changing on some time scale.

Two systems A and B have the same *empirical temperature* if when brought in thermal contact there is no net heat transfer from one to the another. In principle any closed system can be used to define a scale for *empirical temperature*. e.g. a column of mercury marked so that $\theta_m \equiv 0$ at melting point of water and $\theta_m \equiv 100$ at the boiling point of water. This defines the Celsius temperature scale.

Alternatively one can define a temperature based on the pressure and of a fixed volume of gas such as He.:

$$\theta \equiv pV / nR$$

where n is the number of kmoles and R=8300 Jkmole^{-1} K^{-1}. This scale is independent of the gas type provided the gas is close to being ideal and weakly interacting. For real gases this approximates the Kelvin or absolute temperature scale where 0 is absolute zero and water melts at θ=273K. *Absolute temperature* is denoted *T*.

zeroth law of TD

If a system A is in thermal equilibrium with B and also with a system C then B and C are in thermal equilibrium. e.g. suppose A is our mercury thermometer.
It can be used to measure the temperature of any two systems. Provided the measured temperatures are the same then the two systems are in equilibrium. In TD this transitive property of thermal equilibrium is not a logical consequence but an empirical observation.

One may be tempted to think of temperature as measure of amount of energy since for an ideal gas the mean kinetic energy scales with temperature but this is incorrect. In many familiar systems the total energy of a system changes but the *T* remains constant. Where?

Internal Energy U

For every object there exists a state quantity called internal energy (U). A state quantity is a function of *state variables* which define the system (e.g . p, V for a gas). U can change in different ways depending the system and how it is coupled to the environment around it. In an *isolated system*:

$$\Delta U = W$$

where W is the *work done on the object* e.g. by gradual compression of a gas.
For a reversible process

$$\delta W = -pdV, \quad W = -\int_{V1}^{V2} pdV$$
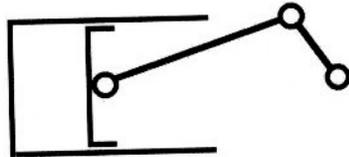
In a *closed system* (where the mass of the body is fixed) but where heat may be exchanged with the environment

$$\Delta U = Q + W$$

where Q is the amount of heat entering the system through the walls. The first law is basically energy conservation. Note W and Q are not state functions since they are not functions of state variables (e.g. p, V for a gas with N_A kmoles). In differential form **the first law of TD** is:

$$dU = \delta Q - pdV$$

For example one can move the system from points A to C through different paths (through D or B) which involve different amounts of work and heat transfer but the total energy at the end being the same.
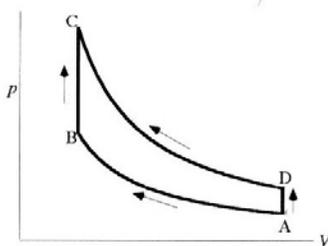
Reversible Process

A *reversible process* can be *returned to its original state* without any net heat transfer to the environment. (As we will see this means that there is no change in total *entropy S*).

Consider an isolated system initially at volume V_1 allowed to expand slowly against a piston to occupy a volume $V_2 = V_1 + V_0$.
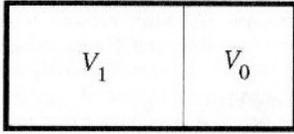
If the piston is frictionless the gas does work on the piston and the internal energy decreases. However we can do that same amount of work on the system, increase U and return the gas to its original state. Thus it is reversible. Suppose the piston is massless and offers no resistance such that the gas freely expands to V_2. We can then compress the gas back to V_1. Why is this not a reversible process?

Enthalpy H

$$H \equiv U + pV$$
$$dH = dU + pdV + Vdp = \delta Q + Vdp$$

Enthalpy is a state function and is useful in any process which can be carried out at constant
pressure. e.g. heating a volume of gas at constant pressure. Suppose you boil a volume of water under constant pressure: Then you require an amount heat
$$\delta Q = \Delta U + p\Delta V = \Delta H \text{ where } \Delta U \text{ is the latent heat.}$$

Heat Capacities C_V and C_p

Heat capacity is the amount of *energy* (not heat) required to raise the temperature of the system. It can be measured at constant volume or more typically at constant pressure.

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V \qquad C_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$$

If we supply a small amount of heat at constant V

$$dU = \delta Q - pdV \qquad\qquad dH = \delta Q + Vdp$$
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\delta Q}{\partial T}\right)_V \quad \text{similarly} \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\delta Q}{\partial T}\right)_p$$

If you measure empirically the heat capacities you can determine most of the other thermodynamic
variables or state functions such as :

$$U(V,T) = \int_0^T C_V dT$$

$$H(p,T) = \int_0^T C_p dT$$

Entropy S

In thermodynamics the change in entropy of a system at temperature T and *fixed volume V*:

$$dS \equiv \frac{\delta Q}{T}$$

where an amount of heat δQ is transferred slowly to the body. For larger amounts of heat where the temperature
changes from T_i to T_f one can compute the total change in entropy:

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT$$

The total amount of entropy at temperature T can be determined by taking $T_i = 0$ $T_f = T$.
Using the **third law of TD** that S=0 at T=0.

$$S_{tot}(V,T) = \int_0^T \frac{C_V}{T} dT$$

Unlike Q the entropy S is a state function.

The **second law of TD** states that the entropy of an isolated system always increases. For example consider an isolated system consisting of two bodies Σ_1 and which are brought into thermal contact in such a way that an amount of heat δQ flows from Σ_1 to Σ_2 (with no change in their respective volumes)

Then $dS = \dfrac{\delta Q}{T_2} - \dfrac{\delta Q}{T_1}$

$\qquad = 0$ if $T_1 = T_2$

$\qquad > 0$ if $T_1 > T_2$

Another important TD state quantity is the **Free Energy.**
$F = U - TS$

We will show later that a system with constant volume in thermal equilibrium with a heat bath will tend to minimize its free energy.

Similarly the **Free Enthalpy**:
$$G = H - TS$$
A system at constant pressure in contact with a heat bath will tend to minimize its free enthalpy. Thus in thermodynamics there is no need to know anything about the constituent parts in order to characterize its thermodynamics behaviour. You can simply measure things such as its heat capacity, determine all state quantities as a function of some minimal set of state variables (e.g. p,V for a gas) .

In contrast in SM we start from a knowledge of the microscopic constituents and derive all the thermodynamic state quantities U, T, S, F etc using a single assumption.

Summary: