Thermodynamics and Statistical Mechanics

These notes mention a few key thermodynamic concepts that would be useful in the course. Look them up in the book if you need some brushing up.

Thermodynamics: A phenomenological description of properties of systems at or very near thermal equilibrium. Developed as a widely applicable **general** axiomatic formalism in the nineteenth century.

Statistical Mechanics: An attempt to derive the the thermodynamic description from the underlying microscopic description. Started late in the nineteenth century, but got developed fully in the last one.

Statistical mechanics not only computes the relationships between macroscopic variables, but also provides us with probability distributions of microscopic variables.

A Brief and Informal Recap of Thermodynamics

Let us start with a simple example: homogeneous gas/fluid. What are some of the **state variables** that characterize the system? One could think of amount of gas (in moles), volume, pressure, temperature, total energy, ...

The state variables can be separated into two categories, **intensive** and **extensive**. If I just combine more of the same, intensive variables don't change whereas the extensive variables change proportionally to the amount of material. For example, pressure, temperature,... would be intensive but volume, energy,.. would be extensive.

The state variables need not all be independent. For example, for ideal gas, the equation of state, $PV = nRT$ (with P, pressure, V volume, T the temperature in Kelvin, n, no. of moles of gas and R, the gas constant), provides a relation between state variables.

A system has reached **thermal equilibrium** when the state variables don't change anymore. If two systems are in contact via a thermally conducting wall, and the state variables of the systems do not change, they are in thermal equilibrium.

Laws of Thermodynamics

Zeroth Law of Thermodynamics: If systems A and B are in thermal equilibrium and if systems B and C are in thermal equilibrium, then systems A and C are in thermal equilibrium.

This law leads to a state variable playing the role of **temperature**. One often uses the ideal gas with the equation of state, $PV = nR\theta$, to define a temperature θ.

Thermodynamics often deals with quasi-static processes, where at every moment the system is arbitrarily close to equilibrium and its state could be described by usual state variables.

First Law of Thermodynamics: There is a state variable U, such that its change is given by

$$\begin{aligned} dU &= \text{đ}Q - \text{đ}W \qquad (1) \\ \text{Change in total internal energy} &= \text{Heat added -Work done by the system} \end{aligned}$$

For a homogeneous fluid, $\text{đ}W = PdV$ for quasi-static changes.

For the example of a gas in a cylinder with a piston, PdV is the macroscopic bit of the mechanical work done on the gas molecules. The thermal part of the energy is in fact mechanical work too, but it is transferred by microscopic vibrations of the walls, interacting with the gas molecules.

This is just energy conservation. In statistical mechanics, heat flow has to do with the changes in the probability distribution in configuration space.

Note that there are no state variables like Q or W. The terms $\text{đ}Q$,$\text{đ}W$ are just differential forms that are **inexact**, meaning they do not represent changes of a function of state variables (which would correspond to and **exact differential**).

For an exact differential one-form

$$\omega = \sum_i f_i dx_i = d\phi(x_1, \ldots, x_n)$$

we have

$$f_i = \frac{\partial \phi}{\partial x_i} \Rightarrow \frac{\partial f_j}{\partial x_i} = \frac{\partial f_i}{\partial x_j}.$$

The last condition could be written as the exterior derivative of ω, $d\omega = 0$.

Example: PdV is not exact but $PdV + VdP = d(PV)$ is.

There is more to thermodynamics than just energy conservation. One never sees a pond freeze on a hot summer day by releasing heat to its environment. This is dealt with in the second law of thermodynamics. There are many different ways to state it. Here is Clausius' version.

Second Law of Thermodynamics: No process is possible whose sole result is to transfer heat from a system at lower temperature to a system at higher temperature.

[Higher and lower as in ideal gas temperature θ for example.]

By some rather elegant arguments, one could show that the second law implies existence of a state variable **entropy** (Clausius), denoted S, such that, for **reversible** processes,

$$dS = \frac{đQ}{T}$$

where T defines the **absolute temperature**. Entropy is an extensive quantity.

What does one mean by a reversible process? The process whose direction could be reversed by infinitesimal changes in the parameters.

Note that for a thermally isolated reversible process, $dS = 0$. It turns out that the second law is equivalent to stating that for a thermally isolated system, $\Delta S \geq 0$.

There is one relation that we would need soon, in our study.

$$dU = TdS - PdV \Rightarrow dS = \frac{1}{T}dU + \frac{P}{T}dV.$$

Hence

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}.$$

This relation would be essential for calculating the temperature from something called the microcanonical ensemble.

Third Law of Thermodynamics: The difference of entropy between states go to zero as temperature goes to zero.

An example would be the entropy difference in a paramagnetic system (think of it a as a bunch of independent spins) at a fixed temperature at two different magnetic fields. As that fixed temperature goes down, so does the difference of entropy.

Nernst proposed a third law of thermodynamics, having to do with what happens to entropy as system goes to absolute zero of temperature. His statement, made more stringent by Planck, states that $S \to 0$ as $T \to 0$. Note that this version was proposed in early 1900's after Boltzmann's microscopic definition of absolute entropy in the later half of nineteenth century. In traditional thermodynamics one can only talk of the difference of entropy, since the second law just defines changes in entropy. This law is an assumption about the density of states of the system near the lowest energy state (the ground state). The third law holds good for many systems but does not have to be universally so. Your understanding of the rule would be clearer once we do a few examples of entropy calculation from the microscopic description of particular systems.

Thermodynamic Potentials

$$dU = TdS - PdV$$

tells us that if we knew the functional dependence of internal energy on entropy and volume, $U = U(S, V)$, then we immediately know temperature and pressure, by taking partial derivatives, and we could derive every other thermodynamic variable. In fact, knowing $S = S(U, V)$, more directly accessible from statistical mechanics, is as powerful, obviously.

Here are a few other quantities.

Enthalpy:

$$H = U + PV$$

$$dH = dU + d(PV) = TdS - PdV + PdV + VdP = TdS + VdP$$

For constant pressure processes, as in many chemical reactions, the heat released is related to the enthalpy change.

As one can see, knowing $H = H(S, P)$, one could easily derive other quantities. However, this relation is not easily accessible from statistical mechanics. We will look at two other quantities that are more relevant to our subject.

Helmholtz free energy:

$$F = U - TS$$

$$dF = dU - d(TS) = TdS - PdV - TdS - SdT = -SdT - PdV$$

Calculating the Helmholtz free energy as a function of temperature and volume: $F = F(V,T)$, would be one of our standard routes to getting the other thermodynamic quantities. For example,

$$P = -\left(\frac{\partial F(V,T)}{\partial V}\right)_T$$

would give us the equation of state for fluids.

Gibbs free energy:

$$G = U - TS + PV$$

$$dG = dU - d(TS + PV) = TdS - PdV - TdS - SdT + PdV + VdP = -SdT - VP$$

Note that the convenient thing to know is $G = G(P,T)$, namely Gibbs free energy as a function of two intensive variables, pressure and temperature.