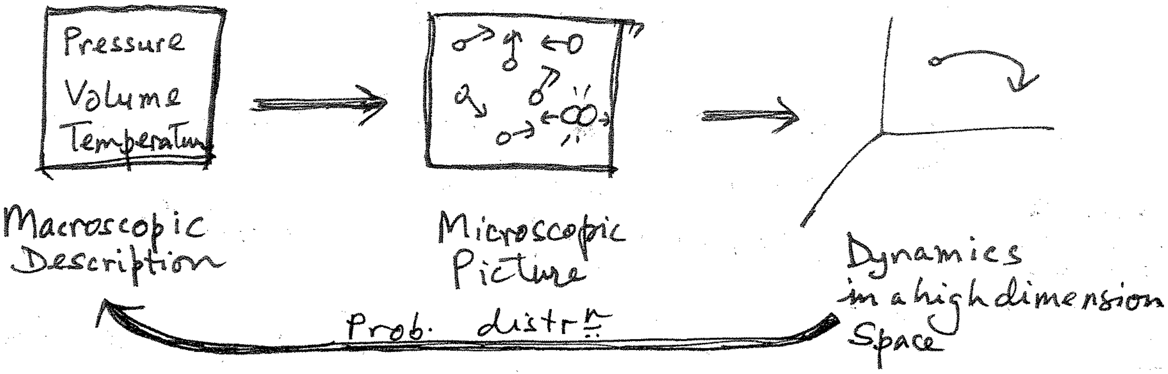
Thermodynamics Review + Microscopic Picture

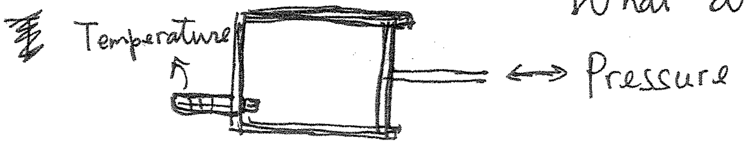
Thermodynamics: A phenomenological description of great generality to describe properties of thermal equilibrium. Developed greatly in the nineteenth century

Statistical Mechanics: An attempt to describe the microscopic basics underlying the thermodynamic description. Started late in nineteenth century but developed fully in the last.

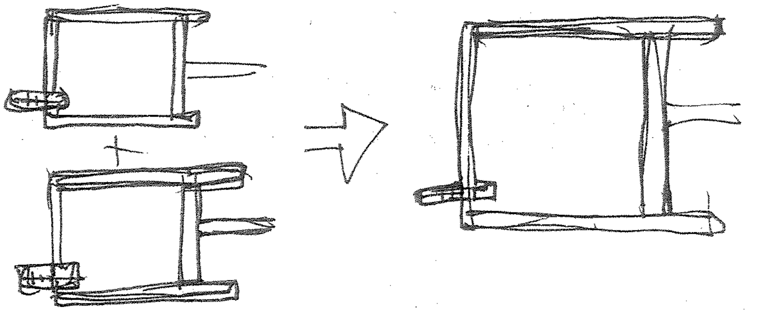


Statistical Mechanics not only computes relations between macroscopic variables, it also tells us about distribution of microscopic variables.

Let us start with this very simple example: Homogeneous gas/f
What are some of the state variables

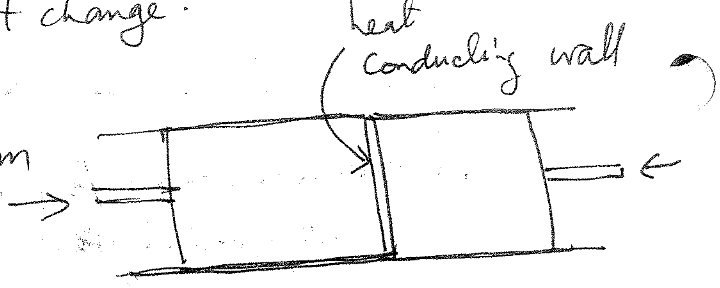


Temp, Pressure
intensive



Volume
extensive

Equilibrium : ~~[illegible]~~ when the state variables don't change.



Thermal Equilibrium of two systems : →

when the state varibles don't change despite thermal contact.

The zeroth law of Thermodynamics :

If ~~system~~ A & B are in thermal ~~contact~~ equilibrium
and if " B & C " " " "
then " A & C " " " "

⇒ Gives rise ~~[illegible]~~ to a state variable playing the role of temperature. One often uses the ideal gas, with eqn of state $PV = nR\theta$ to define one temp θ.

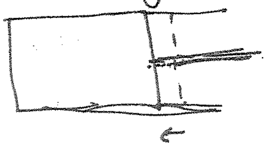
Thermodynamics often deals with quasistatic processes where in that process every point on the path is arbitrarily close to equilibrium and could be described by usual state variables

The first law of Thermodynamics

There is a state ~~[illegible]~~ variable, the total internal energy ~~[illegible]~~ U, such that its change

$$dU = \overset{\text{heat}}{\text{đ}Q} + dW^{\text{work}}$$

For homogeneous fluids $$\text{đ}W = -\underset{\substack{\uparrow \\ \text{Pressure}}}{P}\,dV \leftarrow \text{Volume}$$



This is just energy conservation. In statistical mechanics, it will turn out that the heat flow part has to do with the changes in the ~~[illegible]~~ ~~distrib~~ probability distribution of the configurations

Note that there is no state variable like Q or W.

$đQ$, $đW$ are just differential forms that are not exact, meaning they are not the changes of any function:

A diffl 1-form $\omega = \sum_i f_i \, dx_i = d\phi$
implies $f_i = \partial\phi/\partial x_i \Rightarrow \frac{\partial f_i}{\partial x_j} = \frac{\partial f_j}{\partial x_i}$
$\Leftrightarrow d\omega = 0$ [curl free in 3d]

For example $p\,dV$ is not exact
but $p\,dV + V\,dp = d(PV)$ is.

But as far as thermaldynamics is concerned there is more [redacted] than just energy conservation. One never sees a pond freeze on a hot summer day by releasing heat to [redacted] its environment.

This is [redacted] dealt in the second law of thermodynamics. There are many different ways to state it. One of them is the Clausius'.

The second Law of Thermodynamics

No process is possible whose sole [redacted] result is to transfer heat from a system at lower temperature to a system at higher temperature

[Higher and lower as in ideal gas]

By some rather elegant / convoluted excercise using Carnot cycles and what not, one can show that the second law implies that there is as state variable S, such that for reversible processes

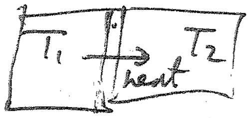
$$dS = \frac{dQ}{T}$$

T being another state variable that depends only on temperature. T is defined to be the absolute temperature and made to match the ideal gas temperature to fix a scale, leading to a definition of entropy (Clausius).

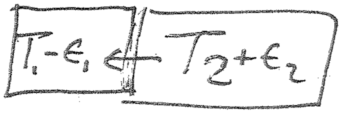
[Our goal in the stat mech course would be to give ~~some~~ a microscopic definition of entropy (Boltzmann). It will be related to the abundance of microscopic states at a particular energy.
Comments of macroscopic irreversibility vs microscopic reversibility. Coin tossing example.]

What do I mean by reversible process? These are defined as processes whose direction could be reversed by infinitesimal changes of parameters

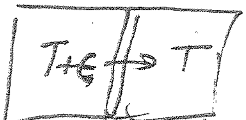
Example



$T_1 \gg T_2$ Not reversible



Impossible



Reversible

Note that for a reversible process in a thermally and otherwise isolated system $dS=\frac{1}{T}dQ=0$. It turns out that the second law is equivalent to stating that for that isolated system $\Delta S \geq 0$.

BTW, we need one relation for our later study

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

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

This eqn would be us in the discussion on the microcan and canonica

Nernst proposed a third law of thermody having to do with what happens as we rea absolute zero of temperature. He proposal, ma (more stringent by Planck is) that $S \to 0$ as $T \to 0$. It will turn out that this is an assumption about density of states near the lowest energy state (the ground state) of the system. This is often true but does not have to be universally so. More about this later.

So far we have talked about quantities like P, V, T, U and S. Now it is time to define a few other quantities which come very handy in Statistical mechanics. These are the various thermodynamic Potentials

The Thermodynamic Potentials

In an isolated system the entropy never decreases. Under some assumptions one could then expect it to be the maximum possible subject to the constraints of energy conservation and equation of state.

For systems that are not thermally insulated but are under other constraints (const pressure, volume/temperature) one can often define (like entropy) quantities that would be minimized. These go by the name of thermodynamic potentials. This is why these quantities were invented, historically.

$$dU = đQ + đW = TdS - PdV$$

Enthalpy $H = U + PV$

$$dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$$
$$= TdS + VdP$$

Note that if the system is under constant pressure everywhere (as is the case in many chemical reactions) and the temperature is held fixed, then $\Delta H = T\Delta S (= Q$, the heat flowing in, provided everything happened reversibly).

~~A thermally isolated system subject to mechanical interaction with the environment, one~~

More crucial for Statistical Mechanics are Helmholtz free energy $F = U - TS$

$$dF = dU - TdS - SdT = TdS - PdV - TdS - SdT$$
$$= -SdT - PdV$$

So,

$$\boxed{P = -\left(\frac{\partial F}{\partial V}\right)_T} \quad \text{and} \quad \boxed{S = -\left(\frac{\partial F}{\partial T}\right)_V}$$

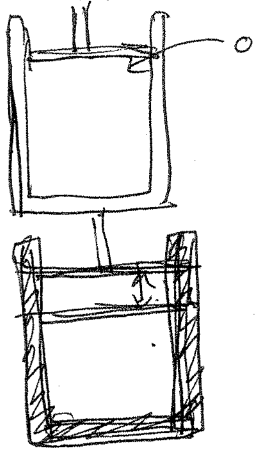
Thus if we know $F(V,T)$. We can practically calculate all quantities. For example

$$U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V$$

Another interesting quantity is the Gibbs free energy $G = U - TS + PV$

$$dG = -SdT + VdP$$ leading to similar relations.

One last comment on Gibbs Free energy.



Adding one more particle at fixed P & T.

Now [illegible] we know

$$G(P,T,N) = N g(P,T)$$

since P, T are intensive variables.

[illegible] [illegible]

~~In general~~ Now let us take internal energy $U(S, V, N)$

$$\boxed{dU = TdS - PdV + \underset{\uparrow}{\mu} dN} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

defined to be chemical potential

Now if we just at one more particle at fixed P, and all extensive quantities will change by the fraction 1/N.

$$\text{So} \quad dU = \frac{1}{N} U \qquad dS = \frac{S}{N} \qquad dV = \frac{V}{N}$$

$$\Rightarrow \mu = dU - TdS + PdV = \frac{U - TS + PV}{N}$$

$$= \frac{G}{N} = g$$

So the chemical potential is just the Gibbs free energy per particle.

An alternate of writing the same eqn. is

$$T\,dS = dU + P\,dV - \mu\,dN$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}}$$

This eqn is of great utility when we come to discuss the grand canonical ensemble.

Apart from calculating the usual state variables we are often interested in [redacted] response to changes. For example specific heal measure the amount of heat getting in the system for unit change of temperature

At [redacted] volume

$$C_V = \frac{dQ|_V}{dT}$$

[redacted]

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

[redacted]

At const pressure

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

One could also calculate compressibility $k = -\frac{\Delta V/V}{\Delta P}$

At fixed temp, [redacted] $k_T = -V^{-1}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{[redacted]}{V\left(\frac{\partial P}{\partial V}\right)_T} = \frac{1\ [redacted]}{V\left(\frac{\partial^2 F}{\partial V^2}\right)_T}$

Adiabatic comp $k_S = -V^{-1}\left(\frac{\partial V}{\partial P}\right)_S = \frac{[redacted]}{V\left(\partial^2 U/\partial V^2\right)_S}$

similar relations.