

Thermodynamics - empirical ~~axioms~~ axioms and consequences, logical systems.

Some notions are counter-intuitive, such as entropy.

Stat mech gives insight into thermodynamics.

$P(E) \propto \exp(-PE)$  - cf. Paul's talk.

Here, constant energy.

Point particle is a cubic box, 3 dimensions.

What state can this particle take?

Wikipedia "particle in a box."



Schrodinger's equation, relativistic quantum mechanics.

$q$  = state of the particle. Solution of Schrodinger is

$\frac{p^2}{2m} = E_q = \frac{\hbar^2}{8mL^2} (l_x^2 + l_y^2 + l_z^2) + \phi$   $\hbar$  = Planck's constant,  $m$  = mass.

"kinetic energy"

quantum mechanical solution.

interaction energy.

$l_x = 0, \pm 1, \pm 2, \dots$   
 $l_y = \dots$   
 $l_z = \dots$

quantum numbers

$l_x, l_y, l_z$  is a microscopic state of the system.

Many states for one energy.

~~Add~~ Add more particles, assume no interaction.

Total energy = sum of ~~all these terms~~ energies of individual particles.

Contradictory assumption: particles can change energy (via walls).

But energy is still conserved.

Above soln. does not tell us pressure in terms of no. of particles.

Stat mech does this. Consider number of particles  $\sim 10^{23}$ .



Thermodynamics is only valid for large numbers of particles.

They are probabilistic laws

$E = \text{energy}$

$N = \text{no. of particles}$

$V = \text{volume}$

do not determine state - many states, same energy.

We would need to know how state changes.

1) If we wait long enough, history becomes irrelevant.

System is in equilibrium.

2) All states corresponding to a given energy are equally likely.

Note that states with an even distribution are more likely to be observed, since there are many ways to get the same kind of situation.

Mathematicians are trying to justify this using dynamical systems.

Let  $\Gamma = \#$  <sup>microscopic</sup> states of the system corresponding to a particular  $E, N, V$ .

Entropy,  $S = k \ln \Gamma$ ,  $k$  constant.

Boltzmann.

makes units correct.



As  $E$  increases,  $\infty$  does  $\Gamma$ , hence  $S$ .

$$S = S(E, N, V)$$

So  $S$  is monotonic in  $E$ .

$$\text{So } E = E(S, N, V)$$

$$E = \sum_{\text{particles}} E_{\text{particle}}$$

$$E_{\text{particle}} = \frac{\text{const.}}{V^{2/3}} (l_x^2 + l_y^2 + l_z^2)$$

But  $\Gamma$  does not depend on  $V$  here.

$$E = E(S, N, V) \text{ (smoothed out version)}$$

$$dE = \left. \frac{\partial E}{\partial S} \right|_{N, V} dS + \left. \frac{\partial E}{\partial N} \right|_{S, V} dN + \left. \frac{\partial E}{\partial V} \right|_{S, N} dV$$

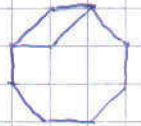
$\downarrow$   $\downarrow$   $\downarrow$   
 $T$   $\mu$   $p$   
 chemical potential



fugacity =  $e^{-\mu/kT}$  = how much energy required to introduce another particle into the system.

$pV = NkT$  ideal gas.

$\int pV = NkT$



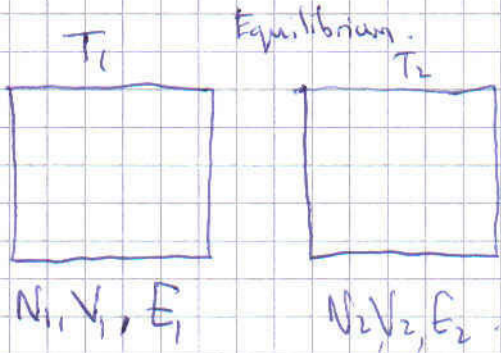
Pauli  $\Gamma = \Gamma_{N,V}(E)$



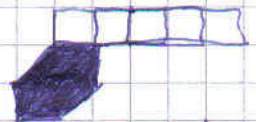
Heisenberg's uncertainty principle  
 $\Delta E \approx \frac{h}{\tau}$

[Note: At a constant temperature, energy can vary a little]

$k$  = Boltzmann constant, so units of  $T$  are Kelvin.



Put together for a short time so small amt. of energy is exchanged



We cannot compute energy after separation.

$\Gamma_{+b}(\text{combined system}) = \Gamma_{1b} \Gamma_{2b}$   
 $\Gamma_{+a} = \Gamma_{1a} \Gamma_{2a}$

$\Rightarrow S = S_1 + S_2$

Energy will flow when  $\Gamma_{+}$  increases.

$S$  also increases.

$\therefore S$  is maximum when system is in equilibrium.

$d(E_1 + E_2) = 0$ , so  $T_1 \delta S_1 + T_2 \delta S_2 = 0$

$\delta(S_1 + S_2) = 0$  as  $S$  is at a maximum.

Hence  $T_1 = T_2$ . Similarly for  $\mu$  and pressure.

~~At  $S_{max}$ ,  $\mu_{max}$ .~~

Two things is thermal equil.  $\Leftrightarrow$  temperatures are the same.

Equilibrium is Transitive. (Zeroth Law) of Thermodynamics.

(i.e.) notion of temperature which helps you decide if objects are in thermal equilibrium.