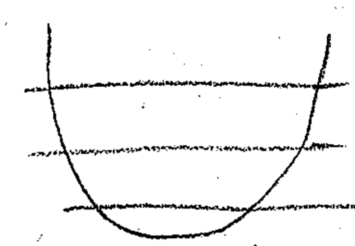
Quantum Statistics

— If we have many particles, what is the distribution of their energies? That is, how many have what value of E?

- For example, this room is a 3D infinite square well (approximately). + Each air molecule is in one of the energy eigenstates $\psi = A \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$, w/ energy $E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$
  - \# For a given fixed # of molecules N and a given fixed total energy E, we are asking how many have a given (n_x, n_y, n_z)
- A very simple example: N particles in harmonic oscillator. Remember each particle has energy $\hbar\omega(n + 1/2)$



  + Try $N=2$ particles with $E_{tot} = 4\hbar\omega$ $(n_1 + n_2 = 3)$.
    Possibilities:
    $(n_1, n_2) = (0,3), (3,0), (1,2), (2,1)$
  + Try $N=5$ particles with $E_{tot} = \frac{25}{2}\hbar\omega$ $(n_1 + n_2 + n_3 + n_4 + n_5 = 10)$
    Possibilities $(2,2,2,2,2)$, $\underbrace{(0,2,2,2,4), (2,0,2,2,4), \ldots}_{20 \text{ possibilities}}$

    $\underbrace{(3,3,2,2,0) \ldots}_{30}$ ....
  + It can be easier to write the # of particles in each state. (occupancy numbers)
    For $N=5$ example, $(N_0 = 0, N_1 = 0, N_2 = 5, \ldots)$
    $(N_0 = 1, N_1 = 0, N_2 = 3, N_3 = 0, N_4 = 1, \ldots)$, $(N_0 = 1, N_1 = 0, N_2 = 2, N_3 = 2, \ldots)$
  + Notice that some sets of occupancy numbers are more common. For very large N, E, one is most likely by a lot. That is the way particles are distributed in thermal equilibrium

- There are two possible subtleties:
  + A single particle energy E_i can go with more than one state. The degeneracy d_i is the number of states with that energy.
  + We've assumed the particles are distinguishable. This is ok if their wavefunctions don't overlap much, but it doesn't work in general. Identical particles are indistinguishable in quantum. 2 cases: bosons can share the same state, fermions cannot (ie, any state can have at most ~~1~~ of a set of identical fermions)

- How to count: we need to know the # of ways to get each set $\{N_i\}$ of occupation numbers, then maximize it
  - For N distinguishable particles, the # of ways to get $(N_1, N_2, \ldots)$ can be calculated as follows: (example of cards)
    + There are $N!$ ways to order the N particles. (N choices for 1st spot, $N-1$ for 2nd, etc...). The 1st N_1 go into the 1st energy, etc.
    + You've over counted b/c the order of the N_i particles doesn't matter, so we need to divide by $N_1! N_2! \ldots$
    + In each energy level, each particle has d_i choices of state to go into, so multiply by a factor of $d_i^{N_i} \ldots$
    + Final counting is $N! \prod_i d_i^{N_i}/N_i!$
  - For identical fermions, the ordering of the N particles doesn't matter b/c they are indistinguishable. All that matters is
    + The number of ways to put N_1 particles into d_1 states (for energy E_1) is (as above) $d_1!/N_1!(d_1-N_1)!$ (order the states then the 1st N_1 get 1 particle each, but the order of those and the left out ones doesn't matter)

+ The total is therefore $\prod_i \frac{d_i!}{N_i!(d_i-N_i)!}$

- For identical bosons, you only worry about putting N_1 particles in d_1 states, etc, but now more than 1 can go in each state.
  + Think of the d_1 states as boxes. Start at box 1, drop in some particles, move to box 2, etc. You end up dropping N_1 particles and making (d_1-1) moves between boxes.
  + That's N_1+d_1-1 items, N_1 are "drops" and (d_1-1) are "moves". Then, as before, there are $(N_1+d_1-1)!/N_1!(d_1-1)!$ orders
  + Total is $\prod_i (N_i+d_i-1)!/N_i!(d_i-1)!$

- To find the maximum, we'd just differentiate w.r.t. the N_i.
  + <u>But</u> we must hold fixed $\sum N_i = N$ and $\sum N_i E_i = E$.
  + We use Lagrange multipliers and take the ln for ease.
  + For distinguishable particles (for example), maximize
$$\ln(N!) + \sum N_i \ln d_i - \sum \ln(N_i!) + \alpha\left[N-\sum N_i\right] + \beta\left[E - \sum N_i E_i\right]$$
w.r.t. N_i, α, and β (latter just conserve N, E)
  + For large values, use Stirling's approximation $\ln(z!) = z\ln z - z$
  + We find
$$\ln d_i - \ln N_i - \alpha - \beta E_i = 0 \Rightarrow N_i = d_i e^{-\alpha-\beta E_i}$$
  + The <u>number</u> <u>per</u> <u>state</u> is the <u>Maxwell-Boltzmann distribution</u> $n(E_i) = e^{-\alpha} e^{-\beta E_i}$
  + For fermions, $n(E_i) = 1/(e^{\alpha} e^{\beta E_i}+1)$ (<u>Fermi-Dirac</u>)
  + For bosons, $n(E_i) = 1/(e^{\alpha} e^{\beta E_i}-1)$ (Bose-Einstein)

- The physical interpretation
  - What do the Lagrange multipliers mean? Answers here, justification later
    + $\beta = 1/k_BT$, where k_B = Boltzmann's constant (8.6×10^{-5} eV/K), T = temperature = determines average particle energy
    + $\alpha = -\mu/k_BT$, where μ = chemical potential controls the number of particles present. μ = energy cost to add a particle
  - Maxwell-Boltzmann distribution.
    + This is our initial air molecule example

$$E_k = \frac{\hbar^2}{2m}\left(\frac{\pi^2 n_x^2}{L_x^2} + \frac{\pi^2 n_y^2}{L_y^2} + \frac{\pi^2 n_z^2}{L_z^2}\right) \equiv \frac{\hbar^2 \vec{k}^2}{2m}$$

    + We have one state per allowed value of $\vec{k}$ but all states of same $|\vec{k}|$ have same energy. Degeneracy is given by volume of a spherical shell of radius k to $k+dk$ (all components >0) with one state per π^3/V of k-space volume. This is

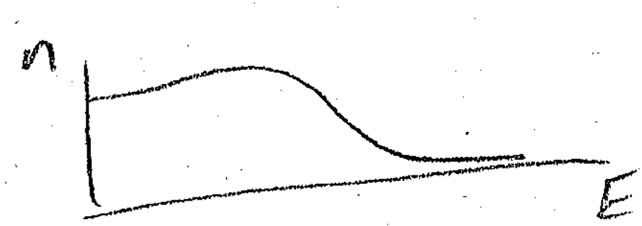
$$d_k = \frac{1}{8}(4\pi k^2 dk)/(\pi^3/V) = \frac{V}{2\pi^2}k^2 dk$$

    + Assuming distinguishable particles,

$$N = \int n(E_k)\,d_k = \frac{V}{2\pi^2}e^{\mu/k_BT}\int_0^\infty e^{-\hbar^2k^2/2mk_BT}k^2 dk$$

Carry out Gaussian integral (show tricks) $\Rightarrow \frac{N}{V} = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} e^{\mu/k_BT}$

    + A similar calculation w/ an extra factor of E_k in integrand gives $E/N = \frac{3}{2}k_BT$
  - Fermi-Dirac Distribution
    + Let's just look at $n(E_i)$



As $T \to 0$, this becomes a step function, $=1$ for $E_i < \mu$, 0 otherwise

+ This means fermions sit in the lowest unoccupied state at low temperatures

- Bose-Einstein distribution
  + Suppose we consider photons in a room. They have the same degeneracy as atoms except x2 for polarizations

$$d_k = \frac{V}{\pi^2} k^2 dk = \frac{V}{\pi^2 c^3} \omega^2 d\omega \text{ in terms of frequency}$$

Energy is $E_\omega = \hbar\omega$.

+ The energy density per frequency range is (# photons)(E/photon)$\left(\frac{\text{degeneracy}}{\text{volume}}\right)$

a $\quad \rho(\omega) = n(E_\omega) E_\omega d\omega = \dfrac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k_B T} - 1)}$

Note: $\mu = 0$ b/c a photon is massless, so there's no energy cost

+ This is the Planck distribution.