L62-Thermal Equilibrium

Friday, February 19, 2016 08:23

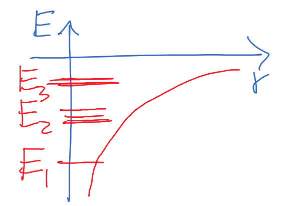
* Reminder: Strategy for multiparticle systems: $\mathcal{H} = \sum_i \mathcal{H}_i(x_i)$

a) determine single-particle states (spectrum) $\mathcal{H}_1 \phi_n(x) = E_n \phi_n(x)$

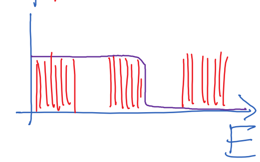
b) distribute N particles into single-particle states $\psi(x_1, x_2 \ldots x_n) = \phi_1(x_1)\phi_2(x_2)\ldots\phi_n(x_n)$

c) [anti]symmetrize identical [fermions] bosons $P_{ij}\psi = \pm\psi$
to determine and count states — Pauli Exclusion Principle

* Examples: a) atom: slater determinant; H-like spectrum



b) solids: i) Fermi gas model ii) Bloch theorem
- give different spectra & degeneracies.
- in ground state, all lowest levels are occupied to E_F



* Excitations should be treated statistically ....

- all we know is the total energy of the system
- there can be many configurations of each particle in individual states.
- Thermal equilibrium: each configuration is equally likely (thermal fluctuations constantly randomly shift configurations.)

skipped

* Example: 3 particles in an infinite square well x_A, x_B, x_C.

$$E = E_A + E_B + E_C = \frac{\pi^2\hbar^2}{2m}(n_A^2 + n_B^2 + n_C^2) \qquad \text{let } E = \frac{\pi^2\hbar^2}{2m}\cdot 363$$

$$363 = \underbrace{\overset{n_A^2 + n_B^2 + n_C^2}{11^2 + 11^2 + 11^2}}_{1 \text{ perm.}} = \underbrace{13^2 + 13^2 + 5^2}_{3 \text{ perm.}} = \underbrace{19^2 + 1^2 + 1^2}_{3 \text{ perm.}} = \underbrace{17^2 + 7^2 + 5^2}_{6 \text{ perm.}}$$

— configurations:

n= 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 . . . .

– configurations:

	$n=$ 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	…
$1\times\ (11,11,11)=$	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	…
$3\times\ (13,13,5)=$	0	0	0	0	1	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	…
$3\times\ (19,1,1)=$	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	…
$6\times\ (17,7,5)=$	0	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0	1	0	0	0	…

– distinguishable particles:

$$P(E_n) = \sum_{\text{config.}} \frac{(\text{degeneracy of config})}{(\text{total \# of states})} \times \frac{(\text{\# particles in state } E_n)}{(\text{total \# of particles})}$$

$n=$	1	5	7	11	13	17	19	
$P_{MB}(E_n)=$	(2	3	2	1	2	2	1)	$/13$

$\sum_n P_{MB}(E_n)=1$

– fermions: only one state: (17, 7, 5) antisymmetrized

$n=$	1	5	7	11	13	17	19	
$P_{FD}(E_n)=$	(0	1	1	0	0	1	0)	$/3$

$\sum_n P_{FD}(E_n)=1$

– bosons: one state in each configuration

$n=$	1	5	7	11	13	17	19	
$P_{BE}(E_n)=$	(2	2	1	3	2	1	1)	$/12$

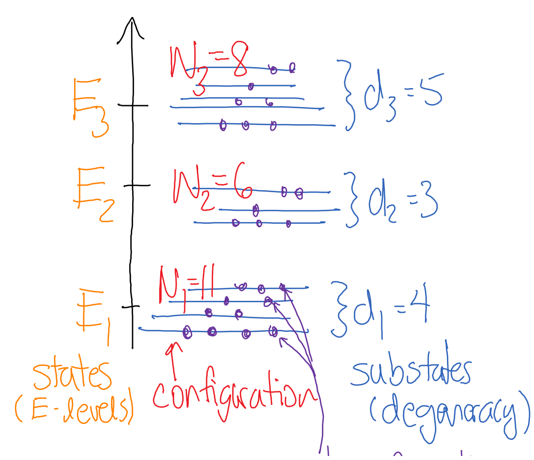
$\sum_n P_{BE}(E_n)=1$

I skipped.

* General case of counting states:

– single particle states:
energy E_1, E_2, E_3 w/ degeneracy d_1, d_2, d_3

– for the N-particle wave function, how many states are there in the configuration $N_1, N_2, N_3 \dots$, where $\sum N_i = N$?



$= Q(N_1, N_2, N_3 \dots)$ "degeneracy" of configuration

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states (E-levels) | configuration | substates (degeneracy)

subconfiguration

a) Distinguishable particles: Maxwell-Boltzman statistics.

$$\#\text{ways to select } N_1 \text{ particles for } E_1 = \binom{N}{N_1} \equiv \frac{N!}{N_1!\,(N-N_1)!} \quad \text{binomial coefficient}$$

$$= \frac{N(N-1)\cdots(N-N_1+1)}{1\cdot 2 \cdots N_1} = \frac{N\,(\text{first choices}) \times [N-1]\,(\text{left overs}) \times \dots}{\#\text{ permutations of selections}}$$

$$\times\ d_1^{N_1} = d_1 \text{ choices for each particle}$$

$\#$ ways to select N_2 particles from $N-N_1$ into d_2 substates

$$= \binom{N-N_1}{N_2} d_2^{N_2} = \frac{(N-N_1)!\, d_2^{N_2}}{(N_2)!\,(N-N_1-N_2)!} \quad \text{and so on.}$$

The total $\#$ of microstates of $(N_1, N_2, N_3 \dots)$ is the product

$$Q_{MB}(N_1, N_2, N_3 \dots) = \frac{N!\, d_1^{N_1}}{N_1!\,\cancel{(N-N_1)!}} \cdot \frac{\cancel{(N-N_1)!}\, d_2^{N_2}}{N_2!\,\cancel{(N-N_1-N_2)!}} \cdot \frac{\cancel{(N-N_1-N_2)!}\, d_3^{N_3}}{N_3!\,\cancel{(N-N_1-N_2-N_3)!}} \cdots \frac{\cancel{N_n!}\, d_n^{N_n}}{N_n!\,(\cancel{0!})}$$

$$= \frac{N!\, d_1^{N_1} d_2^{N_2} \cdots d_n^{N_n}}{N_1!\, N_2!\, N_3! \cdots N_n!} = N! \prod_{i=1}^{n} \frac{d_i^{N_i}}{N_i!} \equiv \binom{N}{N_1, N_2, \dots N_n} \prod_{i=1}^{n} d_i^{N_i}$$

note: $$(x_1 + x_2 + \dots x_n)^N = \sum_{N_1+N_2+\dots=N} \underbrace{\binom{N}{N_1, N_2, \dots N_n}} x_1^{N_1} x_2^{N_2} \cdots x_n^{N_n}$$

multinomial coeff. $= \#$ of ways of splitting N into $N_1, N_2, N_3 \dots$

b) Identical fermions: Fermi-Dirac statistics

Easiest: each substate can have 0 or 1 particles in it. The antisymmetric wavefunction is unique for each subconfiguration of substates.

ways of distributing N_i particles into d_i substates

$$= \binom{N_i}{d_i} = \text{\# ways to split } N_i \text{ into } \{0,1\}$$

$$Q_{FD}(N_1, N_2, N_3 \ldots) = \prod_{i=1}^{n} \binom{N_i}{d_i} = \prod_{i=1}^{n} \frac{N_i!}{d_i!\,(N_i-d_i)!}$$

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c) Identical bosons: Bose-Einstein statistics.

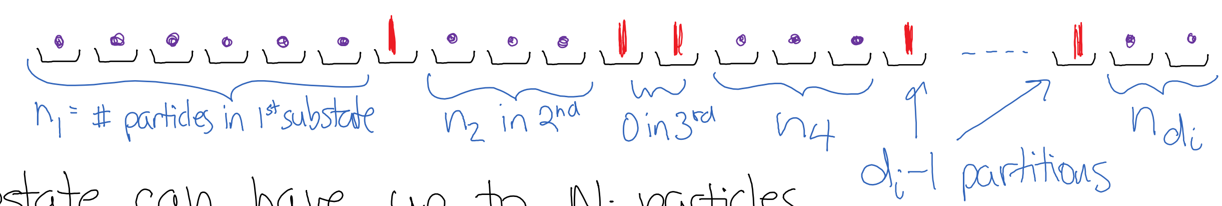
Hardest conceptually: each substate fits unlimited particles
Symmetric wave function unique for each subconfiguration.

ways of distributing N_i particles into d_i substates

$$= \binom{N_i+d_i-1}{d_i-1} = \frac{(N_i+d_i-1)!}{N_i!\,(d_i-1)!}$$

ways of putting d_i-1 partitions "|" into N_i+d_i-1 slots, leaving N_i particles "•"

counting trick:



each substate can have up to N_i particles

$$Q_{BE} = \prod_{i=1}^{n} \binom{N_i+d_i-1}{N_i} = \prod_{i=1}^{N} \frac{(N_i+d_i-1)!}{N_i!\,(d_i-1)!}$$

Next step: use conservation of energy & principle of indifference to determine $n(\varepsilon)$ = probability of being in single-particle state ε