L63-Boltzman Entropy

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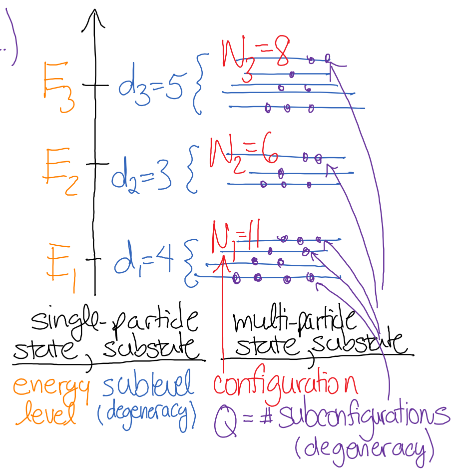
* General case of counting states:

- single particle states: (usually called $g_1, g_2, g_3, \ldots$)
  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 $N_1, N_2, N_3 \ldots$, where $\sum N_i = N$?

  $= Q(N_1, N_2, N_3, \ldots)$ "degeneracy" of configuration.
  usually called $W(N_1, N_2, N_3 \ldots)$



* Strategy to determine the "most likely" configuration:
  note: as $N \to \infty$ "most likely" → "only plausible"
  then we obtain "the" distribution $n(\varepsilon) = N_n/d_n$ = average # particles/sublevel
  for the energy level $\varepsilon = E_n$ (for total #particles N, energy E)

  Minimize $G(N_1, N_2, N_3 \ldots) = \ln(Q)$ with constant $(N, E) = \sum_n N_n (1, E_n)$
  "Entropy" usually labeled $S = kG = k \cdot \ln(W)$ using Lagrange multipliers $(\alpha, \beta) = (\mu, 1)/kT$
  to obtain the statistical distributions

$$n_{MB}(\varepsilon) = \left[e^{(\varepsilon-\mu)/kT}\right]^{-1} \quad n_{FD}(\varepsilon) = \left[e^{(\varepsilon-\mu)/kT} - 1\right]^{-1} \quad n_{BE}(\varepsilon) = \left[e^{(\varepsilon-\mu)/kT} + 1\right]^{-1}$$

This results in the thermodynamic equation

$$dE = \frac{1}{\beta k} dS - \frac{\alpha}{\beta} dN - đW \quad \text{(work)}$$
$$= \underbrace{T\,dS + \mu\, dN}_{\text{stochastic}} - \underbrace{(P\,dV + B\,dM + \ldots)}_{\text{mechanical.}}$$

E, S, N, V, M: extensive
T, μ, P, B: intensive

* Ensembles – we are using the Microcanonical ensemble

	const
– Microcanonical (Boltzman): # of microstates / macrostate.	N, V, E
– Canonical: # of microstates in thermally linked heat reservoir	N, V, T
– Grand Canonical: thermal & diffusive links with reservoir.	μ, V, T

* Calculation of Configuration degeneracy $Q(N_1, N_2, \ldots) \to$ entropy:

a) Distinguishable particles: Maxwell-Boltzman statistics.

first choose the energy levels and then

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

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

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

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

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

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

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

$$= \frac{N!\,d_1^{N_1} d_2^{N_2} \cdots d_n^{N_n}}{N_1!\,N_2!\,N_3! \cdots N_n!} \equiv \binom{N}{N_1,N_2,\ldots N_n} \prod_n d_n^{N_n} = N! \prod_n \frac{d_n^{N_n}}{N_n!}$$

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

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

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

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

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

c) Identical bosons: Bose-Einstein statistics.

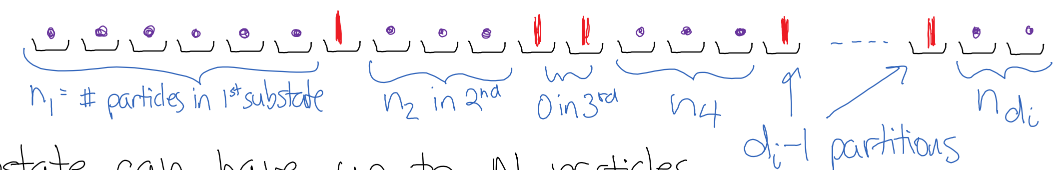
Hardest conceptually: each substate fits unlimited particles
Symmetric wave function unique for each subconfiguration.

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