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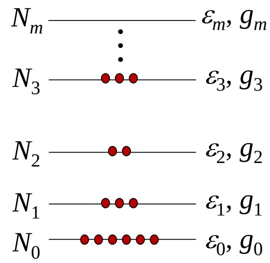
Review Macrostates



- So far we have found the number of microstates $W(N_i)$ in a *given* macrostate, e.g.,

$$W_{Boltzmann}(N_i) \approx \prod_{i=1}^{M} g_i^{N_i} \Big/ \prod_{i=1}^{M} N_i!$$

  - macrostate ≡ given N_i distribution
  - N_i/N ≡ fraction of molecules in i^{th} energy level (N=total # molec.)

- Each "**allowed**" macrostate must meet overall constraints $\sum N_i = N; \ \sum N_i \varepsilon_i = E$

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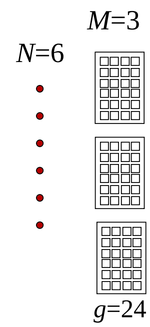
Most Probable Macrostate

- Recall one of our goals is to find total number of possible microstates $\Omega = \sum_{\substack{\text{allowed} \\ \text{macrostates}}} W(N_i)$
- Turns out (show later) that for N large $\ln\Omega \cong \ln W_{max}$ ← for the macrostate with the most microstates
- Also having no reason not too, we will postulate that *all microstates are equally probable*
  - so the macrostate with W_{max} is also the **most probable macrostate** (at equilibrium) *Prob. = W/Ω*
  - and N_i/N for the most probable macrostate will tell us the probability of finding a molecule (particle) in a given energy level (at equilibrium)

Distribution of Microstates

- To demonstrate W_{max} versus Ω, consider putting N particles in M large boxes each with g little boxes
  - for this demonstration we are ignoring energy of each large box
- How many macrostates (N_m distributions)?
  - how many ways to put N things in M big boxes with no limit on N per big box
  - same question as B-E statistics



$$n_{Macro} = \frac{(N+M-1)!}{N!(M-1)!} = \frac{8!}{6!2!} = 28$$

1 = (6,0,0)
2 = (5,1,0) (5,0,1)
3 = (4,2,0) (4,1,1) (4,0,2)
4 = (3,3,0) (3,2,1) (3,1,2) (3,0,3)
5 = (2,4,0) (2,3,1) (2,2,2) (2,1,3) (2,0,4)
6 = (1,5,0) …
7 = (0,6,0) ….

Σ=28

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Distribution of Microstates

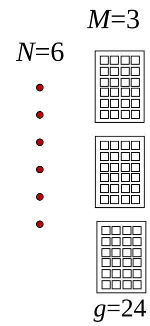
- W for given macrostate?
  - assuming limit of one per little box (F-D)

$$W(N_i) = \prod \frac{g!}{N_i!(g-N_i)!}$$

  - some examples

$$W_{(2,2,2)} = 2.1\times10^7$$
$$W_{(3,2,1)} = W_{(3,1,2)} = W_{(2,3,1)}$$
$$= W_{(1,3,2)} = W_{(1,2,3)} = W_{(2,1,3)} = 1.3\times10^7$$
$$W_{(6,0,0)} = W_{(0,6,0)} = W_{(0,0,6)} = 1.3\times10^5$$

for our equal g's (and no energy issues)
⇒ uniform distribution most probable (*Wmax*)
⇒ nearly uniform distributions very likely



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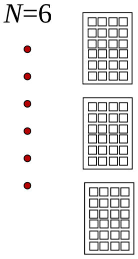
Distribution of Microstates

- How many total microstates?
  - how many ways to put N things in $M\times g$ little boxes with limit of 1 per little box
  - same as F-D statistics

$$\Omega = \frac{(Mg)!}{N!(Mg-N)!} = \frac{72!}{7!65!} = 1.47\times10^{9}$$



- What is mean W?

$$\overline{W} = \frac{\Omega}{n_{Macro}} = \frac{1.47\times10^{9}}{28} = 5.3\times10^{7}$$

- Compare ln Ω, ln W_{max} and ln $\overline{W}$

$$\ln\overline{W} \approx 18;\ \ln W_{max} \approx 19;\ \ln\Omega \approx 21 \ \Rightarrow \boxed{\ln\overline{W} \lesssim \ln W_{max} \lesssim \ln\Omega}$$

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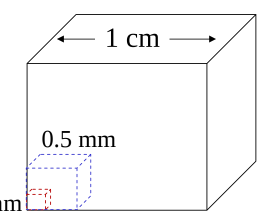
Large N

- **For very large numbers**, these values get closer
  - e.g., N=10[19], M=10[4], g=10[20]

$$\ln W_{max} \approx \ln\Omega \approx 5.1\times10^{21} \ \Rightarrow \ \ln W_{max} = \ln\Omega$$

- Physical interpretation of this example
  - 1 cm^3 region at SATP, $N=10^{19}$
  - 1 Å^3 small box (about size of molec.) $\Rightarrow 10^{24}$ possible "states"
  - "measure" N_i in ~0.5 mm "big boxes" (M~10^4)
  - probability of all molecules in 1 "big" box $=1/\Omega \sim e^{-10^{22}}$
  - probability of uniform distribution ~ 1



Most Probably Energy Macrostate

- So for most macroscopic systems

$$\ln W_{max} = \ln \Omega$$

  - we can focus on ln W_{max} if we want to find ln Ω
- Most probable distribution of particles over energy levels
  - contains nearly all the microstates
  - has nearly 100% probability
  - represents the TD equilibrium particle distribution