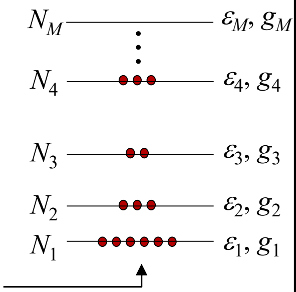
Review Macrostates



- 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*

  principle of equal a priori probability

  so probability of system being in given macrostate = W/Ω

  - thus macrostate with $W_{\max}$ is also the **most probable macrostate** (at equilibrium)
  - 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)

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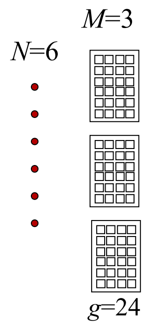
Distribution of Microstates



- To demonstrate $W_{\max}$ versus Ω, consider putting N particles in M large boxes, each with g little boxes
  - for this starting simple demonstration, we are **ignoring energy issues** (simplifies calculations)
- First ask, **how many "macrostates"?** (different N_i 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
  - example: N=6, M=3, g_i=24

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

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

Σ=28 ✓

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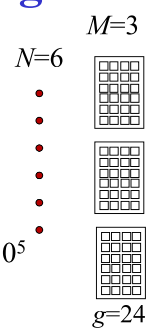
Simplified Example: Comparing *W*



- What is W for a given "macrostate"?
  - assuming limit of one per little box (F-D stats.)

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

  - for our example, some cases
    - all in one i

$$W_{(6,0,0)} = W_{(0,6,0)} = W_{(0,0,6)} \quad = 1.3\times10^5$$

    - nearly uniform

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

    - uniform

$$W_{(2,2,2)} \quad = 2.1\times10^7 = W_{\max}$$

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

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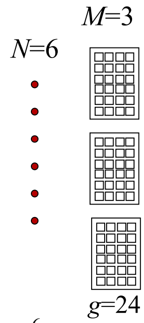
Simplified Example: # Microstates

- 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



$$\Omega = \frac{(Mg)!}{N!(Mg-N)!} = \frac{72!}{6!64!} = 1.56 \times 10^8$$

- What is mean W? $\overline{W} = \frac{\Omega}{n_{Macro}} = \frac{1.56 \times 10^8}{28} = 5.6 \times 10^6$

recall $W_{max} = 2.1 \times 10^7$

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

$\ln \overline{W} \approx 15.5$; $\ln W_{max} \approx 16.9$; $\ln \Omega \approx 18.9$ $\quad$ $\ln \overline{W} \lesssim \ln W_{max} \lesssim \ln \Omega$

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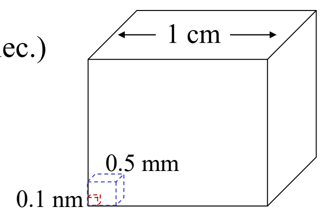
What Happens for Large N

- **For very large numbers**, these values get closer
  - e.g., $N=10^{19}$, $M=8000$, $g=1.25 \times 10^{20}$

$\ln W_{max} = 1.25129... \times 10^{20}$; $\ln \Omega = 1.25129... \times 10^{20} \Rightarrow$ **$\ln W_{max} \cong \ln \Omega$**

- Physical interpretation of this example
  - 1 cm^3 region at SATP, $N \sim 10^{19}$
  - 1 Å^3 small boxes (about size of molec.) $\Rightarrow 10^{24}$ possible locations ("states")
  - how many N_i in larger 0.5 mm "big boxes" ($M = 8000$)
    - probability of all molecules in 1 "big" box ~ $e^{-10^{20}}$
    - probability of exactly same # molec in each "big" box (most probable "macrostate") ~ $e^{-10^{10}}$
    - probability of at least 1.25×10^{15} molec in each "big" box (nearly same, uniform distribution) ~ 1



Most Probable Energy Macrostate

- So for most macroscopic (large) systems, we can use

$$\boxed{\ln W_{max} \cong \ln \Omega}$$

  - we can focus on $\ln W_{max}$ if we want to find $\ln \Omega$
  - note: not saying $\Omega = W_{max}$, just that ln of these values is essentially the same
- Most probable distribution of particles over energy levels
  - contains nearly all the microstates
  - has nearly 100% probability
  - represents the TD equilibrium particle distribution
    - e.g., if we made a measurement of an equilibrium system, it is the distribution we would find 99.999…% of the time