

Distribution over Energy Levels

- Now that we know

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

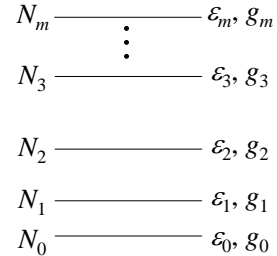
- we have a new question....

- What energy macrostate is the most probable?

- what set of N_i produces W_{\max} ?
- equivalently what set of $N_i \rightarrow (\ln W)_{\max}$?

- To find this, let's start with (corrected) Boltzmann statistics

$$W_{CB}(N_i) = \frac{\prod_{i=1}^M g_i^{N_i}}{\prod_{i=1}^M N_i!} \Rightarrow \ln W_{CB} = \ln \prod_{i=1}^M \frac{g_i^{N_i}}{N_i!}$$



ln W Expression

$$\ln W_{CB} = \ln \prod_{i=1}^M \frac{g_i^{N_i}}{N_i!}$$

- Simplify

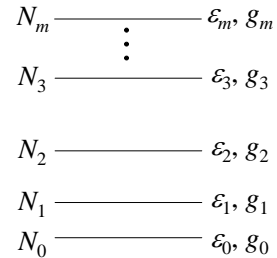
$$\begin{aligned} \ln W_{CB} &= \sum_i \ln \frac{g_i^{N_i}}{N_i!} = \sum_i (\ln g_i^{N_i} - \ln N_i!) \\ &= \sum_i (N_i \ln g_i - \ln N_i!) \end{aligned}$$

- for large x , **Stirling's Formula**

$$\ln x! \cong x(\ln x - 1)$$

$$\ln W_{CB} \cong \sum_i (N_i \ln g_i - N_i \ln N_i + N_i)$$

- Now we need to maximize $\ln W(N_i)$
- how?



Maximizing ln W

$$\ln W = \sum_i (N_i \ln g_i - \ln N_i!) \cong \sum_i (N_i \ln g_i - N_i \ln N_i + N_i)$$

- Maximizing ln W implies a small change in the N_i distribution (δN_i), which would cause a small change in ln W ($\delta \ln W$) is **zero**

$$\delta(\ln W) = \sum_i \frac{\partial(\ln W)}{\partial N_i} \delta N_i = 0 \quad (1) \quad \text{assumes } W \text{ is essentially continuous function of } N_i$$

$$\begin{aligned} \frac{\partial}{\partial N_i} (\ln W_{CB}) &= \frac{\partial}{\partial N_i} \sum_i (N_i \ln g_i - \ln N_i!) \\ &= \sum_i \left(\frac{\partial}{\partial N_i} (N_i \ln g_i) - \frac{\partial}{\partial N_i} \ln N_i! \right) \end{aligned}$$

– with Stirling's Formula

$$\begin{aligned} \frac{d}{dx} \ln x! &\cong \frac{d}{dx} x(\ln x - 1) \\ &\cong \ln x + x(1/x) - 1 = \ln x \end{aligned} \quad \frac{\partial}{\partial N_i} \ln(W_{CB}) \cong \sum_i (\ln g_i - \ln N_i) = \sum_i \ln \frac{g_i}{N_i}$$

Distribution Energy Levels-3

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Maximizing ln W

- Thus requirement to maximize ln W (assuming Boltzmann statistics) becomes $\delta(\ln W) = \sum_i \frac{\partial(\ln W)}{\partial N_i} \delta N_i = 0$

$$\sum_{i=1}^M \delta N_i \ln \frac{g_i}{N_i} = 0 \quad (1')$$

– with constraints

$$\text{Mass} \quad \sum_i \delta N_i = 0 \quad (2)$$

$$\text{Energy} \quad \sum_i \varepsilon_i \delta N_i = 0 \quad (3)$$

- (1', 2', 3') are set of 3 coupled algebraic equations

Distribution Energy Levels-4

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Solution Method

- Powerful method to solve this set
 - Lagrange's Method of Undetermined Multipliers
- Overall approach
 - multiply constraint equations ((2) and (3)) by some constants and add to (1') $\lambda \times 0 = 0$

$$-\alpha \sum_i \delta N_i = 0 \quad (2') \quad -\beta \sum_i \varepsilon_i \delta N_i = 0 \quad (3')$$

$$(1') + (2') + (3') \Rightarrow \sum_{i=1}^m \delta N_i (\ln(g_i / N_i) - \alpha - \beta \varepsilon_i) = 0 \quad (4)$$
 - but α, β arbitrary constants
 - our choice α, β such that for each and every energy level i $= 0$ *so (4) = 0 independent of how we change N_i*
 - resulting equation for each i $\ln \frac{g_i}{N_i} = \alpha + \beta \varepsilon_i \quad (5)$

Energy Level Population Distribution

- So we now have M equations for N_i (let's call them N_i^*) that maximize $\ln W$

$$N_i^* = g_i e^{-\alpha - \beta \varepsilon_i} = g_i e^{-\alpha} e^{-\beta \varepsilon_i} \quad (5) \quad \text{for } \varepsilon_i \uparrow \Rightarrow N_i^*/g_i \downarrow$$

\Rightarrow high lying energy levels tend to be less populated

 - but have $M+2$ unknowns (N_i^*, α, β)
 - so must still satisfy constraints $N = \sum_i N_i^* \quad E = \sum_i \varepsilon_i N_i^*$
- Aside - above deriv. for Boltzmann statistics
 - could repeat for general case (BE or FD statistics) for large N with Stirling's formula

$$\ln W_{\substack{BE \\ FD}} \cong \sum_i \left(N_i \ln \frac{g_i \pm N_i}{N_i} \pm g_i \ln \frac{g_i \pm N_i}{g_i} \right)$$
 - result
$$N_{i \substack{BE \\ FD}}^* = g_i \frac{e^{-\alpha - \beta \varepsilon_i}}{1 \mp e^{-\alpha - \beta \varepsilon_i}} \quad (6)$$

$N_i^* \ll g_i \Rightarrow e^{-\alpha - \beta \varepsilon_i} \ll 1$
Boltzmann limit
and for small ε_i requires $\alpha \gg 1$
 $\Rightarrow (V/N)(2\pi kT)^{3/2} / h^3 \gg 1$

Identifying the Lagrange Multipliers

- To find “useful” expression for N_i^* , need to find α, β
- Most general case, insert (6) for N_i^* into constraint equations

$$N = \sum_i N_i^* \rightarrow N = \sum_i \frac{g_i}{e^{\alpha + \beta \epsilon_i} \mp 1}$$

$$E = \sum_i \epsilon_i N_i^* \rightarrow E = \sum_i \frac{g_i \epsilon_i}{e^{\alpha + \beta \epsilon_i} \mp 1}$$

- could then find α, β for given $N, E, \epsilon_i, g_i \dots$ BUT
- no general analytic solution with this method

Most Probable Energy Distribution

- Using population constraint with **Boltzmann limit**

$$N_i^* = g_i e^{-\alpha} e^{-\beta \epsilon_i} \rightarrow N = \sum_i N_i^* = e^{-\alpha} \sum_i g_i e^{-\beta \epsilon_i}$$

$$\frac{N_i^*}{N} = \frac{g_i e^{-\beta \epsilon_i}}{\sum_i g_i e^{-\beta \epsilon_i}} \quad (7) \text{ Fraction of molecules in } i^{\text{th}} \text{ energy level for most probable macrostate}$$

$$\frac{N_i^*}{N} = \frac{g_i e^{-\beta \epsilon_i}}{Q} \quad Q \equiv \sum_i g_i e^{-\beta \epsilon_i} \quad \text{Partition Function}$$

- So only need to identify β to find most probable macrostate population distribution
 - but first, short detour to look at $\ln W_{\max}$ vs. $\ln \Omega$ now that we have included constraint equations

ln W_{max}

- Recall for Boltzmann limit

$$\ln W \cong \sum_i (N_i \ln(g_i / N_i) + N_i)$$

- For most probable macrostate

$$\begin{aligned} \ln W_{\max} &\cong \sum_i \left(N_i^* \ln \frac{g_i}{N_i^*} + N_i^* \right) && \sum_i N_i^* = N \\ \text{-- from (7)} & && \\ \frac{Q e^{\beta \varepsilon_i}}{N} = \frac{g_i}{N_i^*} & && = \sum_i \left[N_i^* \ln \left(\frac{Q}{N} e^{\beta \varepsilon_i} \right) \right] + N \\ & && = \sum_i \left[N_i^* \ln \left(\frac{Q}{N} \right) + \beta \varepsilon_i \right] + N && \sum_i N_i^* \beta \varepsilon_i = \beta E \\ \ln W_{\max} &= N \left(1 + \ln \frac{Q}{N} \right) + \beta E && \text{(8)} \end{aligned}$$

- so ln W_{max} only depends on macroscopic properties (E, N) and partition function Q (and constant β)

ln W_{max} vs. ln Ω

- Previously illustrated that only small set of macrostates with distribution similar to most probable macrostate contain most of the microstates
- Let's assume there are a finite number (J) of macrostates with same number of microstates as the most probable (and others have negligible amount)

$$\Omega = J W_{\max} \rightarrow \ln \Omega = \ln(J W_{\max}) = \ln W_{\max} + \ln J$$

- as N becomes very large

$$\ln W_{\max} = N \left(1 + \ln \frac{Q}{N} \right) + \beta E$$

$$\beta, E, Q \neq \text{fn}(N) \quad \ln W_{\max} \rightarrow N \quad \text{and } \ln N \ll N$$

$$\ln \Omega \approx N + \ln J \approx N$$

$$\ln \Omega \approx \ln W_{\max} \quad \text{even though } \Omega \neq W_{\max} \quad \text{ln makes it work!!}$$

see V&K p. 107 for further demonstration

Summary – Boltzmann Limit

- **Most probable population distribution** over the energy levels is

$$\frac{N_i^*}{N} = \frac{g_i e^{-\beta \epsilon_i}}{Q} \quad Q \equiv \sum_i g_i e^{-\beta \epsilon_i}$$

- Since the most probable macrostate contains nearly all the microstates, and assuming equal *a priori* probability for each microstate meeting E, N constraints } *fundamental postulate of Stat. Mech.*
 - measurement of N_i produces N_i^* with near certainty
⇒ **thermodynamic equilibrium distribution**

- **Number of microstates**

$$\ln \Omega = \ln W_{\max} = N \left(1 + \ln \frac{Q}{N} \right) + \beta E$$