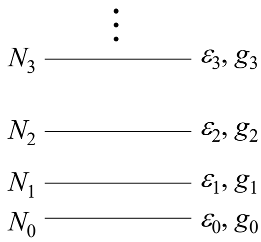
Distribution over Energy Levels

- Now that we know

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

  – 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

$$W_{CB}(N_i) = \frac{\prod_i g_i^{N_i}}{\prod_i N_i!} = \prod_i \frac{g_i^{N_i}}{N_i!} \qquad \Rightarrow \ln W_{CB} = \ln \prod_i \frac{g_i^{N_i}}{N_i!}$$

Copyright © 2009, 2023 by Jerry M. Seitzman. All rights reserved.

ln*W* Expression

$$\ln W_{CB} = \ln \prod_i \frac{g_i^{N_i}}{N_i!}$$

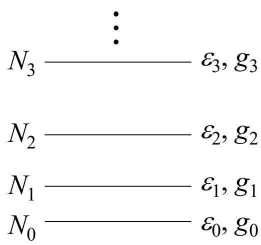
- Simplify

$$\ln W_{CB} = \sum_i \ln \frac{g_i^{N_i}}{N_i!} = \sum_i \left(\ln g_i^{N_i} - \ln N_i!\right)$$
$$= \sum_i \left(N_i \ln g_i - \ln N_i!\right)$$

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

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

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



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

Copyright © 2009, 2023 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering School of Aerospace Engineering

Maximizing ln*W*

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

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

$$\delta(\ln W) = \sum_i \frac{\partial(\ln W)}{\partial N_i}\delta N_i = 0 \quad \textbf{(1)}$$

assumes W is essentially continuous function of N_i

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

$$= \sum_i \left(\frac{\partial}{\partial N_i}(N_i \ln g_i) - \frac{\partial}{\partial N_i}\ln N_i!\right)$$

  - with Stirling's Formula

$$\frac{d}{dx}\ln x! \cong \frac{d}{dx}x(\ln x - 1) \cong \ln x + x(1/x) - 1 = \ln x$$

$$\frac{\partial}{\partial N_i}\ln(W_{CB}) \cong \sum_i \left(\ln g_i - \ln N_i\right) = \sum_i \ln\frac{g_i}{N_i}$$

Copyright © 2009, 2023 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering School of Aerospace Engineering

Maximizing ln*W*

- Thus requirement to maximize ln*W* (assuming Boltzmann statics) becomes

$$\delta(\ln W) = \sum_i \frac{\partial(\ln W)}{\partial N_i}\delta N_i = 0$$

$$\sum_i \delta N_i \ln\frac{g_i}{N_i} = 0 \quad \textbf{(1}'\textbf{)}$$

  - with constraints

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

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

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

Copyright © 2009, 2023 by Jerry M. Seitzman. All rights reserved.

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′)

$\lambda \times 0 = 0$

$$-\alpha \sum_i \delta N_i = 0 \quad \textbf{(2′)} \qquad -\beta \sum_i \varepsilon_i \delta N_i = 0 \quad \textbf{(3′)}$$

$$\textbf{(1′)+(2)+(3)} \quad \Rightarrow \sum_i \delta N_i \underbrace{\left(\ln\left(g_i / N_i\right) - \alpha - \beta\varepsilon_i\right)}_{=0} = 0 \quad \textbf{(4)}$$

  - but α, β arbitrary constants
    - our choice α, β such that for each and every energy level i

so (4) =0 independent of how we change N_i

  - resulting equation for each i

$$\ln \frac{g_i}{N_i} = \alpha + \beta\varepsilon_i \quad \textbf{(5)}$$

Distribution Energy Levels-5

Copyright ©2009, 2023 by Jerry M. Seitzman. All rights reserved.

AE/ME 6765

Energy Level Population Distribution

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

$$\boxed{N_i^* = g_i e^{-\alpha-\beta\varepsilon_i} = g_i e^{-\alpha} e^{-\beta\varepsilon_i}} \quad \textbf{(5)}$$

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

$$\ln W_{\left[\begin{smallmatrix}BE\\FD\end{smallmatrix}\right]} \cong \sum_i \left(N_i \ln \frac{g_i \pm N_i}{N_i} \pm g_i \ln \frac{g_i \pm N_i}{g_i} \right)$$

  - result

$$\boxed{N^*_{i\left[\begin{smallmatrix}BE\\FD\end{smallmatrix}\right]} = g_i \frac{e^{-\alpha-\beta\varepsilon_i}}{1 \mp e^{-\alpha-\beta\varepsilon_i}}} \quad \textbf{(6)}$$

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

Distribution Energy Levels-6

Copyright ©2009, 2023 by Jerry M. Seitzman. All rights reserved.

AE/ME 6765

Georgia Tech College of Engineering
School of Aerospace Engineering

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

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

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

  - could then find α, β for given N, E, ε_i, g_i...BUT
  - no general analytic solution with this method

Copyright © 2009, 2023 by Jerry M. Seitzman.
All rights reserved.

Georgia Tech College of Engineering
School of Aerospace Engineering

Most Probable Energy Distribution

- Using population constraint with Boltzmann limit

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

$$e^{-\alpha} = \frac{N}{\sum_i g_i e^{-\beta\varepsilon_i}}$$

$$\boxed{\frac{N_i^*}{N} = \frac{g_i e^{-\beta\varepsilon_i}}{\sum_i g_i e^{-\beta\varepsilon_i}}}$$

(7) Fraction of molecules in i[th] energy level for most probable macrostate

$$\frac{N_i^*}{N} = \frac{g_i e^{-\beta\varepsilon_i}}{Q} \qquad \boxed{Q \equiv \sum_i g_i e^{-\beta\varepsilon_i}}$$

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

Copyright © 2009, 2023 by Jerry M. Seitzman.
All rights reserved.

Georgia Tech College of Engineering School of Aerospace Engineering

$\ln W_{max}$

- Recall for Boltzmann limit

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

- For most probable macrostate

$$\ln W_{max} \cong \sum_i \left(N_i^* \ln \frac{g_i}{N_i^*} + N_i^*\right) \qquad \sum_i N_i^* = N$$

  – from (7) $\frac{Qe^{\beta\varepsilon_i}}{N} = \frac{g_i}{N_i^*}$

$$= \sum_i \left[N_i^* \ln\left(\frac{Q}{N} e^{\beta\varepsilon_i}\right)\right] + N$$

$$= \sum_i \left[N_i^* \left\{\ln\left(\frac{Q}{N}\right) + \beta\varepsilon_i\right\}\right] + N$$

$$\sum_i N_i^* \beta\varepsilon_i = \beta E \qquad \sum_i N_i^* \ln\left(\frac{Q}{N}\right) = N \ln\left(\frac{Q}{N}\right)$$

$$\boxed{\ln W_{max} = N\left(1 + \ln \frac{Q}{N}\right) + \beta E} \quad \textbf{(8)}$$

  – so $\ln W_{max}$ only depends on macroscopic properties (E, N) and partition function $\boldsymbol{Q}$ (and the constant β)

Distribution Energy Levels-9

Copyright ©2009, 2023 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering School of Aerospace Engineering

Summary – Boltzmann Limit

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

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

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

- **Number of microstates**

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

Distribution Energy Levels-10

Copyright ©2009, 2023 by Jerry M. Seitzman. All rights reserved.