The Boltzmann Distribution

- **The question:** How will molecules distribute themselves over the available energy levels?

- **Constraints:** There are $N = \sum n_i$ molecules and the total energy is $E = \sum \epsilon_i n_i$.

- **The distribution with the most microstates will be the most probable distribution.**

  \begin{align*}
  \epsilon_6 & \quad n_6 \\
  \epsilon_5 & \quad n_5 \\
  \epsilon_4 & \quad n_4 \\
  \epsilon_3 & \quad n_3 \\
  \epsilon_2 & \quad n_2 \\
  \epsilon_1 & \quad n_1 \\
  \text{etc.} & \quad \text{etc.}
  \end{align*}

- **The problem:** To maximize the number of microstates $\Omega$ under the constraints of a constant number of particles $N$ and a constant energy $E$.

- **The method:** Maximize $\ln \Omega$ using the method of Lagrange multipliers and Stirling's approximation.
Derivation of the Boltzmann Distribution

- We wish to maximize $f = \ln \Omega$ under the constraints $g_1 = N - \sum n_i = 0$ and $g_2 = E - \sum \varepsilon_i n_i = 0$.

- The Lagrange formula is

$$\frac{\partial f}{\partial n_j} + \lambda_1 \frac{\partial g_1}{\partial n_j} + \lambda_2 \frac{\partial g_2}{\partial n_j} = 0$$

- Recall that $\Omega = \frac{N!}{n_1! n_2! n_3! ...}$

- $\ln \Omega = \ln(N!) - \ln(n_1!) - \ln(n_2!) - \ln(n_3!) - ...$

- The derivative of this is

$$\frac{\partial (\ln \Omega)}{\partial n_j} = \frac{\partial [\ln(N!) - \ln(n_1!) - \ln(n_2!) ...]}{\partial n_j}$$

$$\frac{\partial (\ln \Omega)}{\partial n_j} = \frac{\partial \ln(n_j!)}{\partial n_j} = -\frac{\partial (n_j \ln n_j - n_j)}{\partial n_j} = -[\ln n_j + n_j(1/n_j) - 1]$$

$$= -\ln n_j$$

- The constraints give:

$$\frac{\partial g_1}{\partial n_j} = \frac{\partial}{\partial n_j}(\sum n_i - N) = 1$$

$$\frac{\partial g_2}{\partial n_j} = \frac{\partial}{\partial n_j}(\sum \varepsilon_i n_i - E) = \varepsilon_j$$
Boltzmann formula derivation (cont.)

- The result is
  \[ \frac{\partial f}{\partial n_j} + \lambda_1 \frac{\partial g_1}{\partial n_j} + \lambda_2 \frac{\partial g_2}{\partial n_j} = 0 \]

\[-\ln(n_j) + \lambda_1 + \lambda_2 \epsilon_j = 0\]

- By tradition we let \( \lambda_1 = \alpha \) and \( \lambda_2 = \beta \). Thus
  \[-\ln(n_j) + \alpha + \beta \epsilon_j = 0\]
  so \( \ln(n_j) = \alpha + \beta \epsilon_j \)

- We now raise \( e \) to the power on each side,
  \[ n_j = e^\alpha \exp(\beta \epsilon_j) \]

We call \( e^\alpha = A \), so that \( n_j = A \exp(\beta \epsilon_j). \)

- We need to evaluate \( A \). We know that \( \sum n_j = N \), so \( \sum A e^{\beta \epsilon_j} = N \). Therefore,
  \[ A = \frac{N}{\sum \exp(\beta \epsilon_j)}. \]
Evaluation of $\beta$

- To evaluate $\beta$ we combine statistical mechanics and thermodynamics. We set

$$S = k \ln \Omega$$

where $S$ is the entropy, $\Omega$ is the "statistical weight" (number of microstates) for the distribution, and $k = \text{Boltzmann constant}$.

- We again apply Stirling's approximation,

$$\ln \Omega = \ln(N!) - \ln(n_1!) - \ln(n_2!) - \ln(n_3!) - \ldots$$

so

$$S = k\{N \ln N - \sum n_j \ln(n_j)\}$$

- Since $n_j = e^{\alpha e^{\beta \varepsilon_j}}$, $\sum n_j \ln(n_j) = \sum n_j (\alpha + \beta \varepsilon_j) = \alpha N + \beta E$ and

$$S = k\{N \ln N - \alpha N - \beta E\}$$

- From thermodynamics, $(\partial S/\partial E)_{V,N} = 1/T$. From above, $(\partial S/\partial E) = -k\beta$, so $(1/T) = -k\beta$. So

$$\beta = -1/kT$$

- The most probable distribution is therefore

$$n_j = \exp(-\varepsilon_j/kT) \frac{N}{\sum \exp(-\varepsilon_j/kT)}$$
The form of the Boltzmann Distribution

• In a complete treatment we must take into account the degeneracies $g_i$ of the energy levels. This gives:

$$n_j = \frac{g_j e^{-\varepsilon_j/kT}}{N \sum g_i e^{-\varepsilon_i/kT}}$$

• The most common form is to take the ratio of the $i^{th}$ and $j^{th}$ energy level populations:

$$\frac{n_i}{n_j} = \left(\frac{g_i}{g_j}\right) e^{-\Delta\varepsilon/kT}$$

• This distribution applies to huge numbers of molecules. Note that the most probable distribution dominates all others.

• It is useful to define the partition function:

$$q = \sum g_i e^{-\varepsilon_i/kT}$$

Note that $q$ is a function of both the energy-level pattern and the temperature. It will increase as $T$ increases.