# Energy Distribution

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## 1 Configurations and Weights

For molecules in a system there is a probability that is will exits in a given energy state. In a system any individual molecule can exist in states with energies from $\epsilon_0$ to $\epsilon_1$ where $\epsilon_0 \equiv 0$. That lowest energy state the **zero-point energy** is the baseline for measuring other energies in the system, and must be accounted for to obtain actual energies of the system.
For a system of $N$ molecule there will be $N_0$ in the $\epsilon_0$ state, $N_1$ in the $\epsilon_1$ state and so on where $\Sigma N_n = N$. The set of populations $N_0, N_1 \cdots$ in the form $\{N_0, N_1 \cdots\}$ is an **Instantaneous Configuration**. For a system of N particles there are $N(N-1)$ configuration total and $1/2N(N-1)$ distinguishable configurations. Systems display the behavior of the state they are most likely to exist in. The number of ways a general configuration can be achieved the **weight** $\mathscr{W}$ is based on number of ways each particle entered its state. For example there are $N_0!$ ways for $N_0$ molecules to be selected. Over the entire configuration that the weight can be given by the following.

$$\mathscr{W} = \frac{N!}{N_0!N_1!\cdots}$$

This is because there are $N!$ ways to select N particles, and for each state with $N_i$ particles there are $N_i!$ ways for those particles to be selected. When summed over the entire system that gives the number of ways to end up with a given configuration.
$\mathscr{W}$ can be approximated with the natural log and using the observation that $\ln x! \approx x\ln x - x$ giving the following.

$$\ln \mathscr{W} = N\ln N - \sum_i N_i \ln N_i$$

### 1.1 Most Probable Distribution

The system will most likely exist in the configuration with the largest weight resulting it's properties matching that of the system. Since weight is a function of $N_i$ that weight can be found by optimizing $\mathscr{W}(N_i)$. This gives the following derivative

$$d\ln \mathscr{W} = \sum_i [\frac{\partial \mathscr{W}}{\partial N_i}]dN_i = 0$$

Given the reality that states will not all share the same energy the configuration with the greatest weight must also satisfy the condition

$$\sum_i N_i\epsilon_i = E$$

meaning the total energy must remain constant as $N_i$ changes. The number of molecules is also fixed meaning that adding a molecule to one state necessitates removing one from another.
Adding the constraints of constant total energy and number of particles to the weight differential

$$\sum_i [\frac{\partial \mathscr{W}}{\partial N_i} + \alpha - \beta\epsilon_i]dN_i = 0$$

where $\alpha$ and $\beta$ are constants. By inserting the equation for $\ln \mathscr{W}$ into this equation the result is

$$\frac{N_i}{N} = e^{\alpha - \beta\epsilon_i}$$

which is close to the Boltzmann Distribution. By there canceling out $\alpha$ the Boltzmann Distribution is arrived at.

$$\frac{N_i}{N} = \frac{e^{-\beta\epsilon_i}}{\sum_i e^{-\beta\epsilon_i}}$$

Here $\beta = 1\ kT$ where k is Boltzmann's constant. The denominator of the equation is called a **partition coefficient**

## 1.2 Relative Population of States

Since the partition coefficient's cancel when the ratio is taken the relative population is given by

$$\frac{N_i}{N_j} = e^{-\beta(\epsilon_i - \epsilon_j)}$$