Statistical Molecular Thermodynamics

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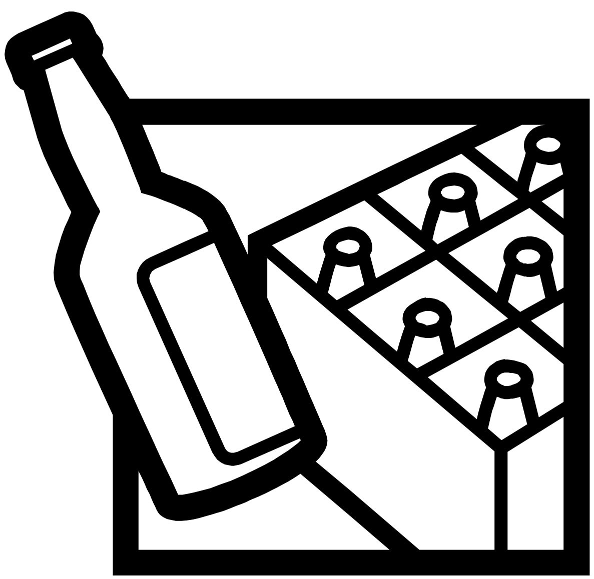
Video 3.2

Boltzmann Population

The Very Large Water Cooler (Ensemble at Fixed Temperature *T*)

Number of bottles having energy E_i given by:

$$a_i = Ce^{-\beta E_i}$$



The Modified Key Question

What is the *normalized* probability that *your* water will be in state i with energy E_i ?

Normalized Probability

$$a_i = Ce^{-\beta E_i}$$

Let A be the *total* number of bottles. The probability p_j that a randomly chosen bottle will be in state j is the number of bottles in state j divided by the total number of bottles.

$$\frac{a_j}{A} = \frac{a_j}{\sum_k a_k} = \frac{Ce^{-\beta E_j}}{C\sum_k e^{-\beta E_k}} = \frac{e^{-\beta E_j}}{\sum_k e^{-\beta E_k}}$$

$$p_j = \frac{a_j}{A} = \frac{e^{-\beta E_j}}{\sum_k e^{-\beta E_k}}$$

p_j is the (normalized) probability that a randomly chosen bottle will be in (quantum) state j

The Partition Function and β

$$Q(N,V,\beta) = \sum_{j}^{\text{states}} e^{-\beta E_j(N,V)}$$

Through the connection between classical thermodynamics and statistical mechanics, one can derive what the quantity β must be, namely

$$\beta = \frac{1}{k_{\mathrm{B}}T}$$

Units: energy^{-1}

So that we may write *Q* as: $Q(N,V,T) = \sum_{j}^{\text{states}} e^{-E_j(N,V)/k_{\mathrm{B}}T}$

Behavior of The Partition Function

$$Q(N,V,T) = \sum_{j}^{\text{states}} e^{-E_j(N,V)/k_{\text{B}}T}$$

For simplicity, let us take the *ground state* to be *non-degenerate* and define its energy as zero. Then all other state energies are positive and

$$Q(N,V,T) = 1 + \sum_{j}^{\substack{\text{excited}\\\text{states}}} e^{-E_j(N,V)/k_{\text{B}}T}$$

Then, as $T \rightarrow 0$, $Q \rightarrow 1$
and, as $T \rightarrow \infty$, $Q \rightarrow$ total number of states

So, the partition function is an effective measure of the "accessible number of energy states"

Behavior of The Partition Function

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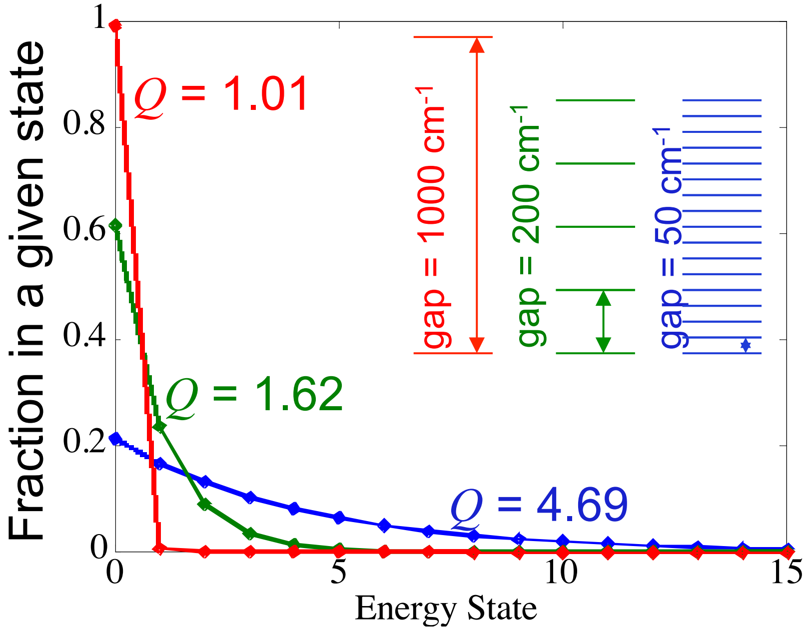
$$Q(N,V,T) = 1 + \sum_{j}^{\substack{\text{excited}\\ \text{states}}} e^{-E_j(N,V)/k_{\mathrm{B}}T}$$

In addition, as the "density of states" → 0, Q → 1
and, as it → ∞, Q → total number of states

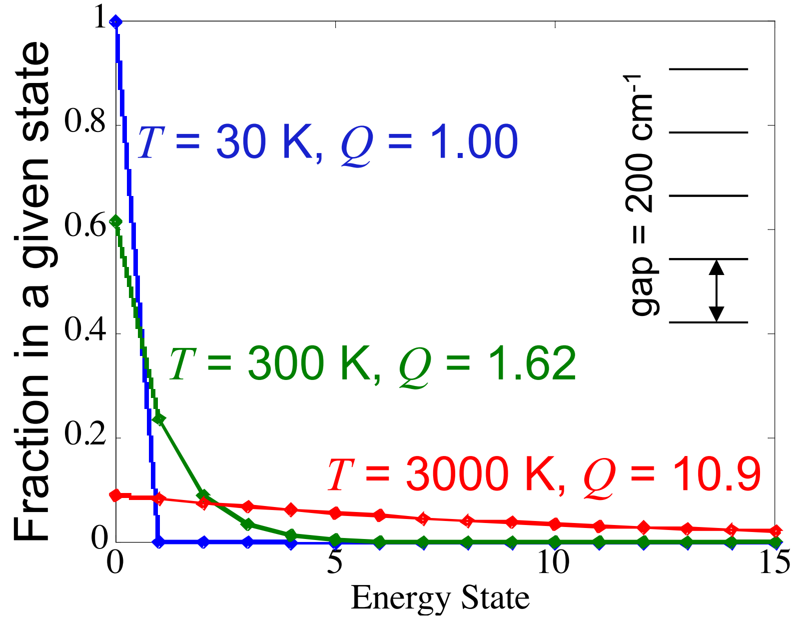
So, the partition function is an effective measure of the "accessible number of energy states"

Behavior of the Partition Function

T = 300 K, $k_B T$ ~200 cm^{-1}



Spacing = 200 cm^{-1}



Boltzmann Population

$$p_j(N,V,T) = \frac{e^{-E_j(N,V)/k_\mathrm{B}T}}{Q(N,V,T)}$$

The above equation can also be derived directly from: $S = k_\mathrm{B} \ln W$

This is one form of the Boltzmann distribution law and is a central result of physical chemistry!