

Foundations of Chemical Kinetics Lecture 2: The Boltzmann Distribution

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Ensembles

- Even without quantum mechanics, matter has some inherently probabilistic qualities.
- In every collision between molecules, energy and momentum are exchanged.
- Even if we knew the positions and momenta of every particle in a container at some time t , our ability to predict the energies, positions and momenta of particles after a few collisions would be essentially zero, except in a statistical sense.
- We treat such systems using **ensembles**, which are large, imaginary sets (approaching infinite size) of copies of a system of interest which have some variables in common and which have been similarly prepared.

The Boltzmann distribution

- Imagine an ensemble of systems all of which are held at the same temperature **or** an ensemble of non-interacting molecules in a container at a fixed temperature T .
⇒ **canonical ensemble**
- According to Boltzmann, the probability that one of these systems (molecules) has energy ϵ_i is given by

$$P(\epsilon_i) = g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right) / q$$

where

g_i is the degeneracy of energy ϵ_i , i.e. the number of different microscopic states (quantum states) that give the same energy,

k_B is Boltzmann's constant,

q is a constant chosen such that $\sum_i P(\epsilon_i) = 1$.

The partition function

- The normalization constant q is called the **partition function**.
- We must have $\sum_i P(\epsilon_i) = 1$, so

$$\sum_i P(\epsilon_i) = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right) / q = 1$$

$$\therefore \frac{1}{q} \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right) = 1$$

$$\therefore q = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

- Depending on context, q is either called the canonical or the molecular partition function.

Meaning of the partition function

$$q = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

- Suppose that, at some temperature of interest, $k_B T \gg \epsilon_i$ for $i \leq n$ and $k_B T \ll \epsilon_i$ for $i > n$.
- For states well below $k_B T$, $\exp(-\epsilon_i/k_B T) \approx 1$.
- For states well above $k_B T$, $\exp(-\epsilon_i/k_B T) \approx 0$.
- Thus,

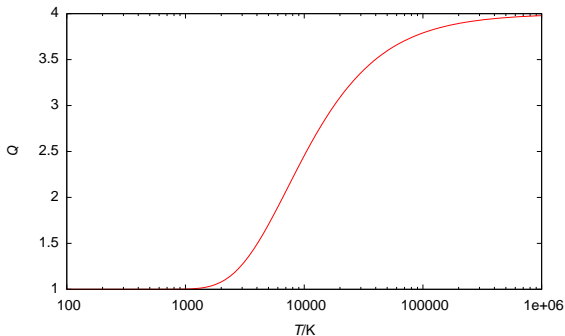
$$q \approx \sum_{i=1}^n g_i.$$

- Roughly speaking, the partition function counts the number of states accessible at temperature T .

Example: The partition function for a two-level system

- Suppose that $\epsilon_1 = 0$, $g_1 = 1$ and $\epsilon_2 = 1 \times 10^{-19}$ J, $g_2 = 3$.

$$q = 1 + 3 \exp\left(-\frac{\epsilon_2}{k_B T}\right) = 1 + 3 \exp(-7243 \text{ K}/T)$$



A minor rewrite of the partition function

We can drop the degeneracy if we sum over quantum states (distinct sets of quantum numbers) rather than over energy levels:

$$q = \sum_{i \in \text{states}} \exp\left(-\frac{\epsilon_i}{k_B T}\right)$$

Separability of partition functions

- Suppose that the molecular energy can be decomposed into a sum of independent contributions, i.e. $\epsilon = \epsilon^{(1)} + \epsilon^{(2)} + \dots$
- Then, using the second form of the partition function, we have

$$\begin{aligned} q &= \sum_i \sum_j \sum_k \dots \exp \left(-\frac{\epsilon_i^{(1)} + \epsilon_j^{(2)} + \epsilon_k^{(3)} + \dots}{k_B T} \right) \\ &= \sum_i \sum_j \sum_k \dots \exp \left(-\frac{\epsilon_i^{(1)}}{k_B T} \right) \exp \left(-\frac{\epsilon_j^{(2)}}{k_B T} \right) \exp \left(-\frac{\epsilon_k^{(3)}}{k_B T} \right) \dots \\ &= \sum_i \exp \left(-\frac{\epsilon_i^{(1)}}{k_B T} \right) \sum_j \exp \left(-\frac{\epsilon_j^{(2)}}{k_B T} \right) \sum_k \exp \left(-\frac{\epsilon_k^{(3)}}{k_B T} \right) \dots \\ &= q^{(1)} q^{(2)} q^{(3)} \dots \end{aligned}$$

The Boltzmann distribution in classical mechanics

- One of the main differences between classical and quantum mechanics is that energy is not quantized in the former theory.
- Accordingly, in classical mechanics, it doesn't make sense to ask for the probability that a molecule has *exactly* energy ϵ . The answer to this question is zero.
- The correct question to ask is what is the probability that a molecule has energy between two specified limits, i.e. what is $P(\epsilon_{\text{low}} \leq \epsilon \leq \epsilon_{\text{high}})$ for some specified values of the two limits?

The Boltzmann distribution in classical mechanics

(continued)

- Define the **density of states** $g(\epsilon)$ such that $g(\epsilon) d\epsilon$ is the number of states between energies ϵ and $\epsilon + d\epsilon$.
- Let ϵ_o be the result of an observation of ϵ . Then,

$$P(\epsilon \leq \epsilon_o \leq \epsilon + d\epsilon) = g(\epsilon) \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon/q$$

or

$$P(\epsilon_{\text{low}} \leq \epsilon_o \leq \epsilon_{\text{high}}) = \frac{1}{q} \int_{\epsilon_{\text{low}}}^{\epsilon_{\text{high}}} g(\epsilon) \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon$$

Classical partition function

- Let \mathcal{A} be the set of allowed energies. This will normally be an interval of energies, possibly semi-infinite.
- Using very similar reasoning to that used to obtain the quantum partition function, we get

$$q = \int_{\mathcal{A}} g(\epsilon) \exp\left(-\frac{\epsilon}{k_B T}\right) d\epsilon$$

The harmonic oscillator model of vibrational motion

- As you may have learned in your previous classes, we can decompose the vibrational motions of molecules into **normal modes**, which to a first approximation are independent of each other.
- Each vibrational mode is approximately harmonic, provided we only consider lower vibrational states.

Potential energy:

$$V(x) = \frac{1}{2}kx^2$$

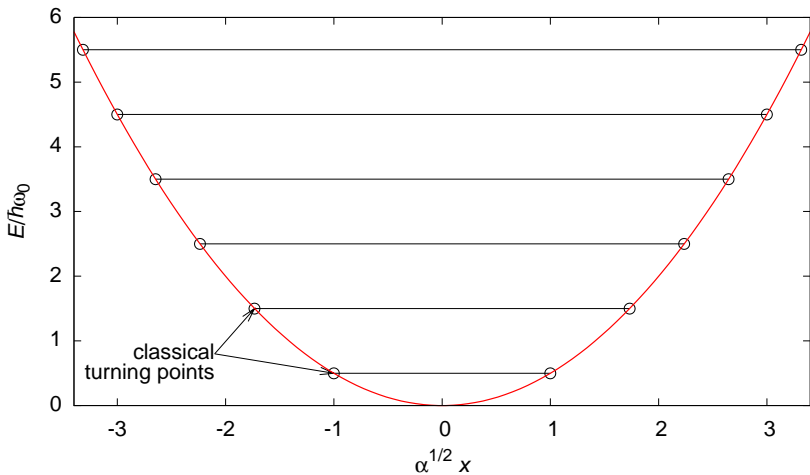
x = vibrational coordinate

k = Hooke's law (spring) constant

- Quantized energy levels:

$$\epsilon_v = \hbar\omega_0 \left(v + \frac{1}{2} \right)$$

Harmonic oscillator energy levels



Example: harmonic oscillator density of states

A “calculation” based on the quantum-mechanical energy

- For the quantum-mechanical harmonic oscillator, the energy levels are equally spaced by $\hbar\omega_0$.
- This means that there is one vibrational mode per $\hbar\omega_0$ of energy.
- The density of states (states per unit energy) is therefore

$$g(\epsilon) = \frac{1}{\hbar\omega_0}$$