Week 10

Topics:

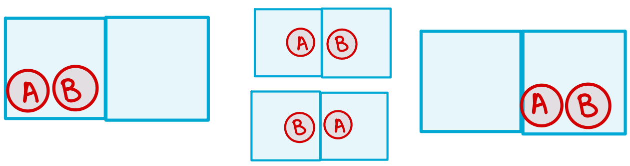
- Boltzmann distribution
- Partition function
- Internal energy and entropy

Statistical thermodynamics links microscopic and bulk properties of materials.
Microscopic: individual molecules
Bulk behaviour: statistical averages over many molecules

Bulk Properties: work, heat, free energy, and entropy.

Molecular Colisions	~1 collision / 10 nanoseconds ; changes with pressure
Conserve energy, linear and angular momentum	conversion of translational, vibrational and rotational energy
	exchange of electronic energy (high temperatures, excited molecules)

Microstates:
Given W **microstates** at a particular energy, probability of finding the system in a particular **microstate** is $p = 1/W$ We seek the most likely configuration

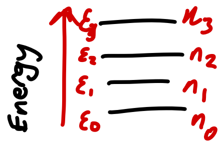


Different states have different energies, we take ε_0 as the lowest state (E=0) and compare all other higher energies relatively. $\varepsilon_0 := \{E = 0\}$

Instantaneous configuration fluctuates with time because populations change.

Set of populations $n_0, n_1, \ldots$ in the form $\{n_0, n_1, \ldots\}$ describes system's instantaneous **configuration**.

To obtain **internal energy**, U, may have to add a constant to calculated energy of system. For example, if considering vibrational contribution to **internal energy**, then must add the total **zero-point energy** of any oscillators in sample.



Macroscopic state can be generated from equivalent **microscopic states**.
Number of different microscopic states giving rise to a macroscopic state is the **weight**.

General Case

Weight of configuration in which n_0 molecules are in ε_0, n_1 molecules are in ε_1, n_2 molecules are in ε_2 *etc. is:*

$$W = \frac{N!}{n_0!n_1!n_2!....}$$

total number of molecules

number of molecules in ε_1.

number of molecules in ε_0.

Example

N! = 10!

If there are 10 molecules, what is the weight of configuration in which there is 5 molecules in the ground state ($n_0 = 5$), 3 molecules in the first excited state ($n_1 = 3$), and 2 molecules in the second excited state ($n_2 = 2$)?

$$W = \frac{(5+3+2)!}{5!3!2!} = \frac{10!}{1440} = \frac{3628800}{1440} = 2520.$$

Boltzmann Distribution – particle distribution over energy states.

The dominant configuration of particles characterises the properties of the system

$$p_i = \frac{n_i}{N} = \frac{e^{\frac{-\epsilon_i}{kT}}}{\sum_i e^{\frac{-\epsilon_i}{kT}}} = \frac{e^{\frac{-\epsilon_i}{kT}}}{q} = \frac{g_i e^{\frac{-\varepsilon_i}{kT}}}{\Sigma g_i e^{\frac{-\varepsilon_i}{kT}}}$$

prob of finding n_i molecules in state with energy ε_i

number of molecules in state with energy ε_i

total number of molecules

partition function sum

partition function

degeneracy (i.e. 1, 2, 3)

in Jules

Goal: maximise W, whilst keeping total number of molecules constant and total energy of the system constant.

Partition function at a particular temperature is related to the number of occupied states.

Partition function links thermodynamics, spectroscopy, and quantum mechanics.
Partition function can be used to calculate enthalpy, free energy, heat capacities, entropies, and equilibrium constants.

Relative population of levels

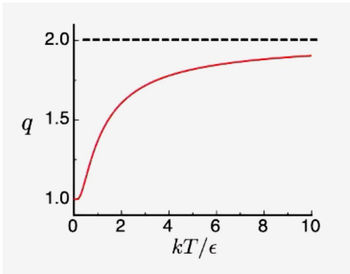
exponential decay

desired / total.

$$p_i = \frac{n_i}{N} = \frac{e^{\frac{-\epsilon_i}{kT}}}{\sum_i e^{\frac{-\epsilon_i}{kT}}} = \frac{e^{\frac{-\epsilon_i}{kT}}}{q}$$

probability, as prior.

partition function.



$$\frac{n_j}{n_i} = \frac{g_j}{g_i} e^{\frac{-(E_j - Ei)}{kT}}$$

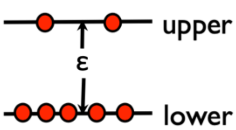
reletave degeneracy dictates probability

As temperature increases, higher energy levels become increasingly populated. (Electronic excitation ⇝ promotion)

vibrational
rotational
translational

Two Level System:

Levels are separated by ϵ_0 .



$$p_i = \frac{n_i}{N} = \frac{e^{\frac{-\epsilon_i}{kT}}}{q}$$ Boltzmann distribution

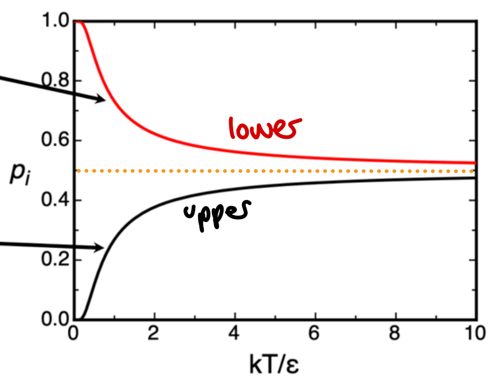
probability of occupation of lower state (e.g. ϵ_0)

$$p_{lower} = \frac{1}{q} = \frac{1}{(1 + e^{\frac{-\epsilon}{kT}})}$$

excited/higher state probability.

$$p_{upper} = \frac{e^{\frac{-\epsilon}{kT}}}{q} = \frac{e^{\frac{-\epsilon}{kT}}}{(1 + e^{\frac{-\epsilon}{kT}})}$$

partition function



asymptote = 0.5
(as $\sum_{i=0}^{2} p_i = 1$)

At low temperature (kT<<ε), lower state is almost exclusively populated (less chance of being populated)

At high temperature (kT>>ε), upper and lower states have almost equal populations

high degree of excitation.