Statistical thermodynamics

- Link to macroscopic thermodynamics from the statistical analysis of molecular properties.
  - Valid for systems in thermal equilibrium
- "System" refers to the macroscopic term
- Microscopic level is populated by "particules" (molecules actually in our case)
- State refers to the "thermodynamic state" or to the "microscopic state", the number of molecules and their energy levels
  - Many microstates (the "ensemble") are compatible with a single thermodynamic state.
  - Ensembles are in constant fluctuation, but the derived macroscopic properties are constant.
  - The value of a macroscopic property is the average of the corresponding microscopic property in the ensemble. Ex. $E = <\varepsilon> = \sum p_i \varepsilon_i$ i: all ensemble microstates. p_i probability of a particle being in the microstate i

Statistical thermodynamics

- Two key ideas
  - Boltzmann distribution predicts populations of states in systems at thermal equilibrium.
  - The derivation of Boltzmann distribution leads naturally to the introduction of partition function.

- Questions:
  - How to interpret partition function and calculate it.
  - How to extract thermodynamic information from the partition function

Statistical thermodynamics

- System composed of N molecules.
  - Total internal energy is constant at E
  - It is not possible to be definite about how that energy is shared between the molecules.
  - Collisions result in the ceaseless redistribution of energy, not only between the molecules but also among their different modes of motion.

- Population of a state
  - the average number of molecules that occupy it. On average there are n_i molecules in a state of energy ε_i.
  - The populations of the states depend only on ε_i that is a function of T

- **All states having the same Energy level (and T) are equally probable**.

Configurations and weights

Instantaneous configurations

Energy

$\varepsilon 2$ ─────

$\varepsilon 1$ ─────

$\varepsilon 0$ ━━━━━ ← *ground state*
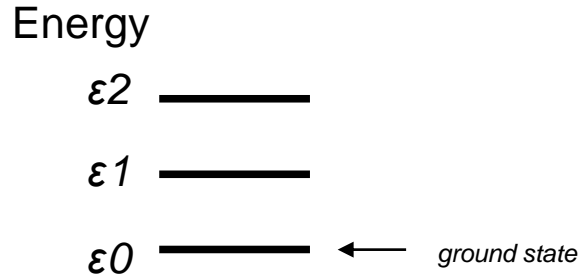
At any instant molecules could occupy one energy level. In this example: $\varepsilon 0, \varepsilon 1,$ or $\varepsilon 2$
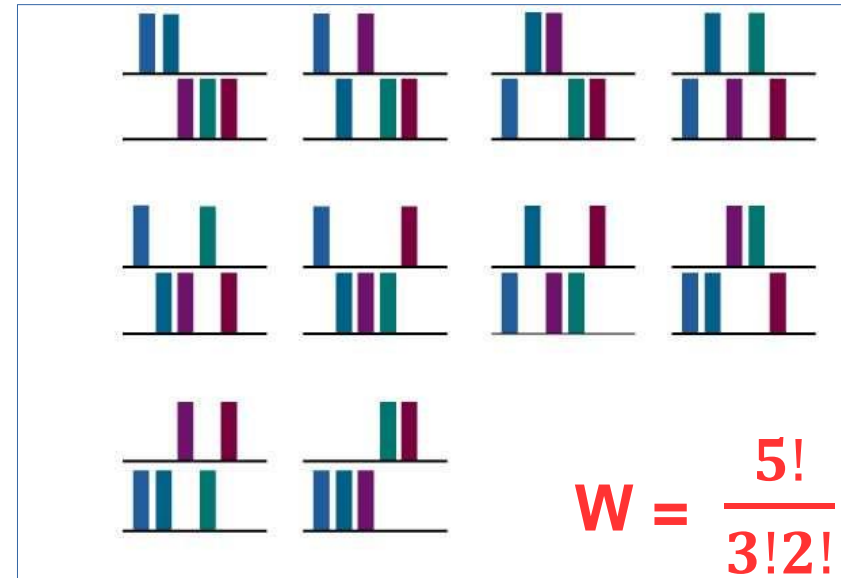
The specification of the set of populations $n0, n1, n2, ...$ in the form $\{n0, n1, n2, ...\}$ is a statement of the **instantaneous configuration** of the system.

Weight of a configuration (W) = N possible microstates for a configuration

$$W = \frac{N!}{n_o! n_1! n_2! n_3!...}$$

For Large N can be written as : $\ln W = N \ln N - \sum_i n_i \ln n_i$

Example: 5 molecules, 2 energy levels

$$W = \frac{5!}{3!2!} = 10$$

Fig. 16.1 Whereas a configuration $\{5,0,0, . . . \}$ can be achieved in only one way, a configuration $\{3,2,0, . . . \}$ can be achieved in the ten different ways shown here, where the tinted blocks represent different molecules.

ATKINS, Chapter 16. Statistical thermodynamics 1, P. 561

Configurations and weights: The optimal distribution

We could find the most probable distribution imposing a system with:

- Constant total number of molecules: $N = \sum_i n_i$
- Constant total energy: $E = \sum_i p_i \varepsilon_i$
- A compatible configuration having the maximum weight $\delta W = 0$

Boltzmann distribution:
$$p_i = \frac{n_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_j e^{-\beta \varepsilon_j}} \qquad \beta = \frac{1}{k_B T}$$

where T is the thermodynamic temperature and k is Boltzmann's constant.

Identical distribution can be obtained from both Kinetic Gas Theory and Statistical Mechanics!!

The molecular partition function

- Boltzmann distribution is a **probability distribution**. It gives the probability of a certain state in function of that state's Energy and the Temperature of the system .

- The normalization term is called **Molecular (canonical) Partition Function**

- Molecular partition function defines the statistical properties of the system from the microscopic states

- The molecular partition function gives an indication of the number of states that are thermally accessible to a molecule at the temperature of the system.
  - At $T = 0$, only the ground level is accessible and $q = g$
  - At very high temperatures, virtually all states are accessible, and q is correspondingly large

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_j e^{-\beta \varepsilon_j}} \qquad \beta = \frac{1}{k_B T}$$

$$Z = \sum_j e^{-\beta \varepsilon_j} = \sum_l g_j e^{-\beta \varepsilon_l}$$

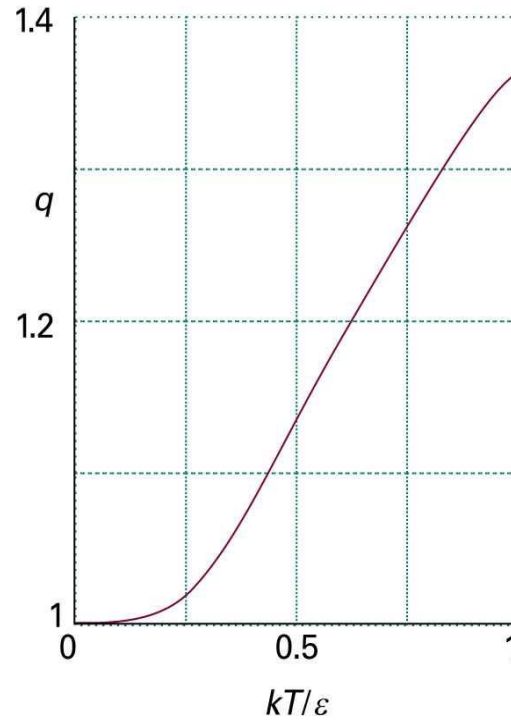Counting either for "j" microstates or for "l" energy levels g_j degenerated
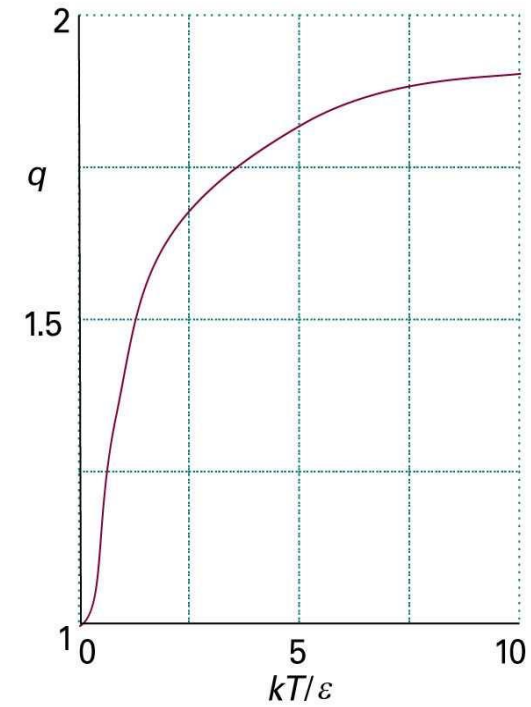
Example: two-level system

$$\varepsilon = \varepsilon \quad \rule{3cm}{1pt}$$

$$\varepsilon = 0 \quad \rule{3cm}{1pt}$$

$$Z = \sum_{i=0}^{\varepsilon} e^{-\beta\varepsilon_i} = 1 + e^{-\beta\varepsilon}$$

small scale

big scale

The partition function for a two-level system as a function of temperature.

Example: two-level system

$$\varepsilon = \varepsilon \quad \rule{3cm}{1.5pt}$$
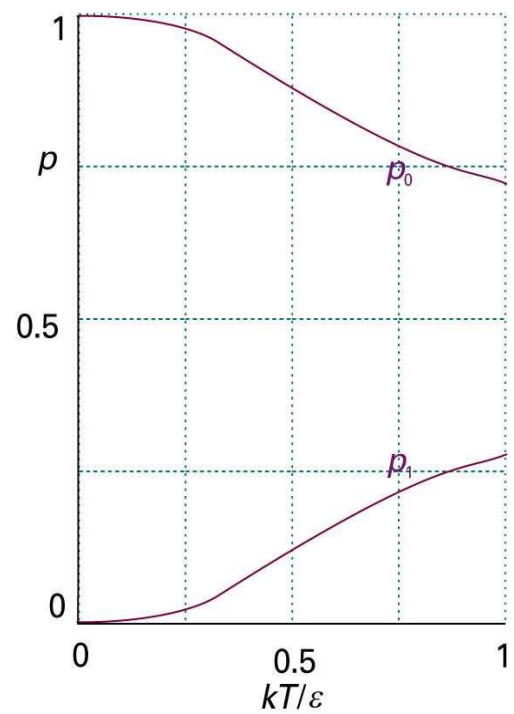
$$\varepsilon = 0 \quad \rule{3cm}{1.5pt}$$

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{q} = \frac{e^{-\beta\varepsilon_i}}{1 + e^{-\beta\varepsilon}}$$

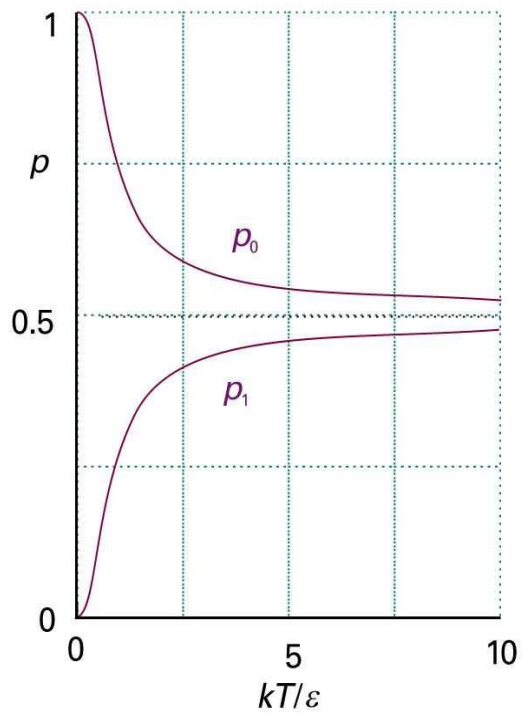$$Z = \sum_{i=0}^{1} e^{-\beta\varepsilon_i} = 1 + e^{-\beta\varepsilon}$$

$$p_0 = \frac{n_i}{N} = \frac{1}{1 + e^{-\beta\varepsilon}}$$

$$p_1 = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}$$

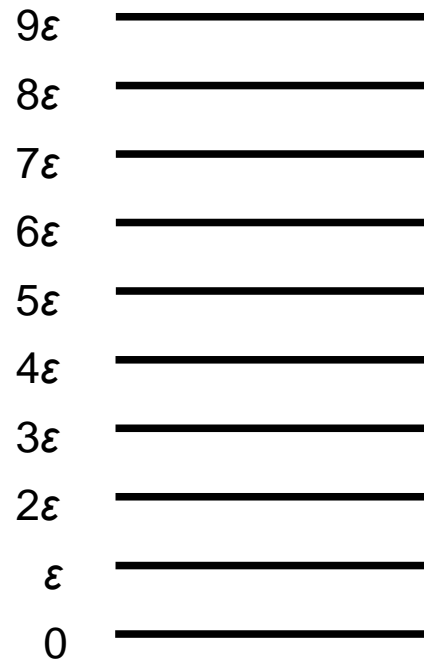*small scale*

big scale

The fraction of populations of the two states of a two-level system as a function of temperature.

Example: uniform distribution of energy levels

A system with equally spaced non-degenerate energy levels.

9ε

8ε

7ε

6ε

5ε

4ε

3ε

2ε

ε

0

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_{i=0}^{9} e^{-\beta\varepsilon_i}}$$

The equally spaced array of energy levels used in the calculation of the partition function.

Temperature (in βε)

Partition fuction

Low temperature   High temperature

βε:	3.0	1.0	0.7	0.3
q:	1.05	1.58	1.99	3.86

Derived Thermodynamic functions

- Internal energy $\quad E = \dfrac{-N}{Z}\left(\dfrac{\partial Z}{\partial \beta}\right) = \dfrac{N}{Z}\sum_i \varepsilon_i e^{-\beta \varepsilon_i}$

- Pressure $\quad\quad\quad P = k_B NT\left(\dfrac{\partial \ln Z}{\partial V}\right)$

- Entropy $\quad\quad\quad S = {}^{E}/_{T} + k_B\, N\ln Z$

- Gibbs $\quad\quad\quad G = -k_B NT\left[\ln Z - \left(\dfrac{\partial \ln Z}{\partial V}\right)\right]$

- "Statistical" entropy

$$S = -k_B N \sum_i p_i \ln p_i$$
$$S = k_B \ln W$$

$$p_i = \frac{1}{Z}e^{-\beta \varepsilon_i}$$

$$\ln p_i = -\beta \varepsilon_i - \ln Z$$

$$-\sum_i p_i \ln p_i = \sum_i (p_i \beta \varepsilon_i + p_i \ln Z) =$$

$$\beta \sum_i p_i \varepsilon_i + \ln Z = \beta E/N + \ln Z$$

$$N\ln Z = -\beta E - N\sum_i p_i \ln p_i$$

$$S = \frac{E}{T} + k_B\, N\ln Z = -k_B N \sum_i p_i \ln p_i$$

$$S = -k_B N \sum_i \frac{n_i}{N} \ln \frac{n_i}{N} = -k_B N\left(\frac{1}{N}\sum_i n_i \ln n_i - \ln N\right)$$

$$\ln W = N\ln N - \sum_i n_i \ln n_i$$

Summary

- Gas theory and statistical thermodynamics can be used to understand the microscopic level

- At the microscopic level, molecules form a complex ensemble of many microstates of different populations and energies

- Macroscopic properties are just averages over such microstates

- Boltzmann distribution gives the probability of particles (molecules) to populate specific microstates

- System thermodynamics functions can be obtained from the molecular partition function.