Chapter 8

Canonical Ensemble (E,V,N)

4. Distribution Function of the Canonical Ensemble

The prefactor $\Omega_2(E)/\Omega(E)$ in (6) is independent of H_1. We may hence obtain the normalization of ρ_1 alternatively by integrating over the phase space of A_1:

$$\rho_1(q(1), p(1)) = \frac{e^{-\beta H_1(q(1),p(1))}}{\int dq(1)\, dp(1)\, e^{-\beta H_1(q(1),p(1))}}, \quad \beta = \frac{1}{k_B T}$$

$$\boxed{\rho_1 = \frac{e^{-\beta H_1}}{\int dq(1)\, dp(1)\, e^{-\beta H_1}}, \qquad \beta = \frac{1}{k_B T}} \tag{7}$$

Boltzmann Factor

The probability P_r of finding the system A_1 (which is in thermal equilibrium with the heat reservoir A_2) in a microstate r with energy E_r is given by

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \text{ Boltzmann distribution} \qquad (8)$$

when rewriting (7) in terms of P_r.

- The number of states $\Omega_2(E_2) = \Omega_2(E - H_1)$ accessible to the reservoir is a rapidly increasing function of its energy.
- The number of states $\Omega_2(E_2) = \Omega_2(E - H_1)$ accessible to the reservoir decreases therefore rapidly with increasing $E_1 = E - E_2$. The probability of finding states with large E_1 is accordingly also rapidly decreasing.

The exponential dependence of P_r on E_r in equation (8) expresses this fact in mathematical terms.

Example: To understand the above concepts in terms of simple numbers?

Suppose a certain number of states are accessible to A_1 and A_2 for various values of their respective energies, as given in the figure, and that the total energy of the combined system is 1007.

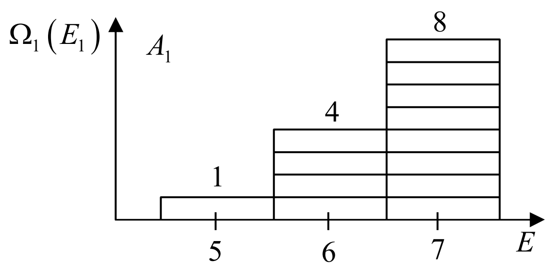
Q. Let A_1 be in a state r with energy 6. E_2 is then in one of the ____ states with energy ____

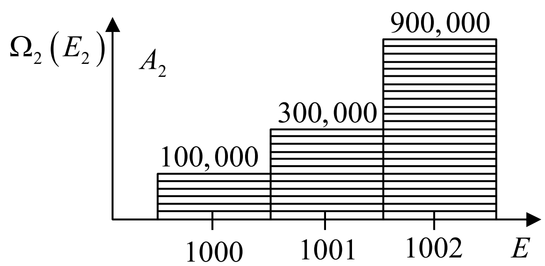
Ans. Let A_1 be in a state r with energy 6. E_2 is then in one of the 3×10^5 states with energy 1001.

Q. If A_1 is in a state γ with energy 7, the reservoir must be in one of the _____ states with energy_______

Ans. If A_1 is in a state γ with energy 7, the reservoir must be in one of the 1×10^5 states with energy 1000.

The number of realizations of states with $E_1 = 6$ the ensemble contains is hence much higher than the number of realization of state with $E_1 = 7$.



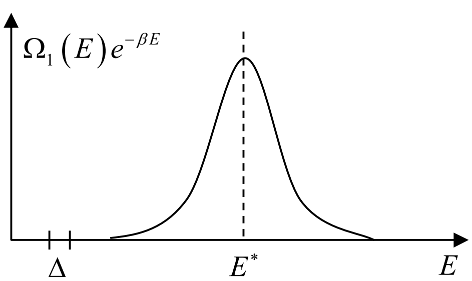


$$P_r = \frac{e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}}$$ Boltzmann distribution

Canonical Ensemble: An ensemble in contact with a heat reservoir at temperature T is called a canonical ensemble, with the Boltzmann factor $\exp(-\beta E_r)$ describing the canonical distribution

Energy Distribution Function: The Boltzmann distribution (8) provides the probability P_r to find an individual microstate r. There are in general many microstates in a given energy, for which

$$P(E) = \sum_{E < E_r < E+\Delta} P_r \propto \Omega(E) e^{-\beta E} \tag{9}$$



is the corresponding energy distribution function.

$\Omega(E) = \Omega_1(E)$ is, as usual, the density of phase space.

- $P(E)$ is rapidly decreasing for increasing energies due to the Boltzmann factor $\exp(-\beta E_r)$
- $P(E)$ is rapidly decreasing for decreasing energies due to the decreasing phase space density $\Omega(E)$.

The energy density is therefore sharply peaked. We will discuss the width of the peak, viz the energy fluctuations.