

according to the probabilistic setting by Boltzmann. To see the property of additivity, suppose that the system is decomposed into two parts in a such a way that the Hamiltonian can be written as

$$H = H_1(\{q_1\}, \{p_1\}) + H_2(\{q_2\}, \{p_2\}), \quad (3.30)$$

where the indices 1 and 2 label the two subsystems. The energy, the number of particles and the volume of the two subsystems must satisfy the relations

$$E_1 + E_2 = E, \quad (3.31)$$

$$N_1 + N_2 = N, \quad (3.32)$$

$$V_1 + V_2 = V. \quad (3.33)$$

To begin with let us imagine that the two systems can exchange energy and particles through the separation wall dividing them, but maintain their respective volumes fixed. The volume in the Γ space of the entire system can be decomposed in terms of the phase-space volumes of the two subsystems as

$$V_{\Gamma}(E, N) = \sum_{N_1=0}^N \frac{N!}{N_1!(N-N_1)!} \sum_{k=1}^{E/\Delta E} V_{\Gamma,1}(E_k, N_1) V_{\Gamma,2}(E-E_k, N-N_1). \quad (3.34)$$

To keep the notation simple, we do not indicate the volume dependence for the time being. The binomial coefficient in the right-hand side of Eq. (3.34) counts the number of ways in which we can assign N_1 particles to the first subsystem and $N_2 = N - N_1$ to the second. Given the uncertainty with which the energy is known, there are $E/\Delta E$ ways in which we can distribute the energy between the two subsystems.

Among all the terms in the two sums over N_1 and k , the biggest contribution comes from the values \bar{N}_1 (and $\bar{N}_2 = N - \bar{N}_1$) and \bar{E}_1 (and $\bar{E}_2 = E - \bar{E}_1$) for which the single term

$$\frac{N!}{N_1!(N-N_1)!} V_{\Gamma,1}(E_k, N_1) V_{\Gamma,2}(E-E_k, N-N_1) \quad (3.35)$$

is maximum.

Since (3.34) is a sum of positive terms,

$$\frac{V_{\Gamma,1}(\bar{E}_1, \bar{N}_1)}{\bar{N}_1!} \frac{V_{\Gamma,2}(\bar{E}_2, \bar{N}_2)}{\bar{N}_2!} \leq \frac{V_{\Gamma}(E, N)}{N!} \leq \frac{NE}{\Delta E} \frac{V_{\Gamma,1}(\bar{E}_1, \bar{N}_1)}{\bar{N}_1!} \frac{V_{\Gamma,2}(\bar{E}_2, \bar{N}_2)}{\bar{N}_2!}, \quad (3.36)$$

we conclude that

$$\begin{aligned} & k_B \ln \frac{V_{\Gamma,1}(\bar{E}_1, \bar{N}_1)}{\bar{N}_1!} + k_B \ln \frac{V_{\Gamma,2}(\bar{E}_2, \bar{N}_2)}{\bar{N}_2!} \\ & \leq k_B \ln \frac{V_{\Gamma}(E, N)}{N!} \\ & \leq k_B \ln \frac{V_{\Gamma,1}(\bar{E}_1, \bar{N}_1)}{\bar{N}_1!} + k_B \ln \frac{V_{\Gamma,2}(\bar{E}_2, \bar{N}_2)}{\bar{N}_2!} + k_B \ln \frac{NE}{\Delta E}. \end{aligned} \quad (3.37)$$

In the thermodynamic limit, $N \rightarrow \infty$, the last term on the right-hand side of (3.37) becomes negligible and we obtain

$$S(E, N) = S_1(\bar{E}_1, \bar{N}_1) + S_2(\bar{E}_2, \bar{N}_2) \quad (3.38)$$

where, in order to satisfy the additivity property with respect to the number of particles, the definition of the entropy (3.29) has been modified as

$$S(E, N) = k_B \ln \frac{V_{\Gamma}(E, N)}{h^{3N} N!}, \quad (3.39)$$

consistently with Eq. (3.21). The conditions fixing the values $\bar{E}_1, \bar{E}_2, \bar{N}_1, \bar{N}_2$ for which the quantity in Eq. (3.35) is a maximum are

$$\frac{\partial}{\partial E_1} (S_1(E_1, N_1))_{E_1=\bar{E}_1, N_1=\bar{N}_1} = \frac{\partial}{\partial E_2} (S_2(E_2, N_2))_{E_2=\bar{E}_2, N_2=\bar{N}_2}, \quad (3.40)$$

$$\frac{\partial}{\partial N_1} (S_1(E_1, N_1))_{E_1=\bar{E}_1, N_1=\bar{N}_1} = \frac{\partial}{\partial N_2} (S_2(E_2, N_2))_{E_2=\bar{E}_2, N_2=\bar{N}_2}. \quad (3.41)$$

From the thermodynamic relation (1.22) we see that the condition (3.40) expresses the thermal equilibrium among the two subsystems,

$$\frac{1}{T_1} = \frac{1}{T_2}, \quad (3.42)$$

and among all the possible energy pairs only one realizes the equilibrium between the two subsystems, assigning to each one its internal energy.

By recalling the other thermodynamic relation (1.30) the condition (3.41) gives the chemical equilibrium among the subsystems:

$$-\frac{\mu_1}{T_1} = -\frac{\mu_2}{T_2} \Rightarrow \mu_1 = \mu_2, \quad (3.43)$$

after using (3.42). The partition of the number of particles at equilibrium is such that each subsystem assumes its Gibbs free energy and their values per particle are equal.