On the generalised ensembles

AI

We consider two systems depicted in fig. 1, where the system 2 plays the role of reservoir (large system), and the system 1 is the system of interest. The total system 1+2 is isolated: it exchanges neither energy nor work with the external world.

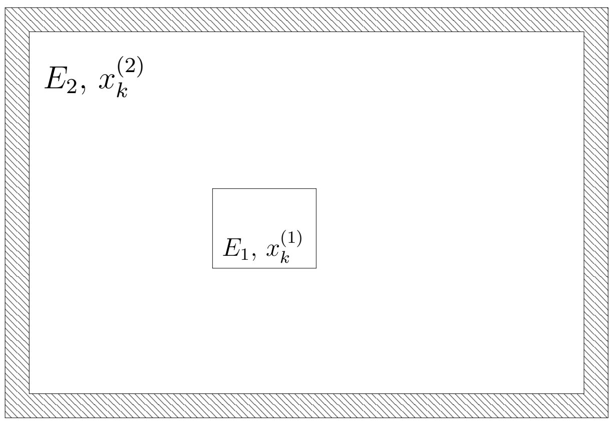

Figure 1: An isolated system partitioned into two subsystems, 1 and 2.

Each of the two systems is described by the extensive variables $(E_i, \{x_j^{(i)}\})$, where $i = 1, 2$ and $x_j^{(i)}$ is a set of extensive variables $x_j^{(i)} = V^{(i)}, N^{(i)}, M^{(i)}, \ldots$.

We allow the two systems to exchange energy and the quantity $x_j^{(k)}$, with k fixed (e.g., we can allow exchange of volume). So, the two systems have equal T and equal X_k, which is the intensive quantity conjugated to x_k (e.g., X_k is the pressure). Since the total system is isolated, we have

$$E_{\rm tot} = E_1 + E_2 = \text{const.} \tag{1}$$

$$x_{k,\rm tot} = x_k^{(1)} + x_k^{(2)} = \text{const.} \tag{2}$$

We also know, that the first law for reversible processes reads

$$T\mathrm{d}S = \mathrm{d}E - \sum_j X_j \mathrm{d}x_j. \tag{3}$$

Using the same approach introduced for the canonical and grand canonical ensemble, and noticing that the total system is isolated, we can estimate the the probability of finding the system 1 in the state with a given value of the energy E_1 and a given value of the extensive variable $x_k^{(1)}$:

$$P_1(E_1, x_k^{(1)}) = \frac{\Omega_1(E_1, x_k^{(1)})\Omega_2(E_2, x_k^{(2)})}{\sum_{\text{all states}} \Omega_1(E_1, x_k^{(1)})\Omega_2(E_2, x_k^{(2)})} = \frac{\Omega_1(E_1, x_k^{(1)})\Omega_2(E_{\text{tot}} - E_1, x_{k,\text{tot}} - x_k^{(1)})}{Z'(T, X_k)}, \tag{4}$$

where in the last equality we have exploited eqs. (1)-(2), and have introduced the generalized partition function $Z'(T, X_k)$ in the denominator. Keep in mind, that similarly to the canonical and grand canonical ensemble, here $\Omega_i(E_i, x_k^{(i)})$ indicates the number of states in system 1 or 2, compatible with the given value of the energy and of the extensive variable. Given the relation between entropy and number of states, we can write

$$\Omega_2(E_{\text{tot}} - E_1, x_{k,\text{tot}} - x_k^{(1)}) = \exp\left[\frac{1}{k_B} S_2(E_{\text{tot}} - E_1, x_{k,\text{tot}} - x_k^{(1)})\right]. \tag{5}$$

Given that the system 2 is large, the quantities E_1, and $x_k^{(1)}$ are small with respect to the total energy and the total extensive quantity, so we can expand the rhs of eq. (5) in a Taylor series up to the first order in E_1, and $x_k^{(1)}$, thus obtaining

$$S_2(E_{\text{tot}} - E_1, x_{k,\text{tot}} - x_k^{(1)}) \simeq S_2(E_{\text{tot}}, x_{k,\text{tot}}) - \left.\frac{\partial S_2}{\partial E_2}\right|_{x_k^{(2)}} E_1 - \left.\frac{\partial S_2}{\partial x_k^{(2)}}\right|_{x_k^{(2)}} x_k^{(1)} \tag{6}$$

$$= S_2(E_{\text{tot}}, x_{k,\text{tot}}) - \frac{E_1}{T} + \frac{X_k x_k^{(1)}}{T}, \tag{7}$$

where in the last equality we have exploited eq. (3). Thus, eq. (4) can be written as

$$P_1(E_1, x_k^{(1)}) = \frac{\Omega_1(E_1, x_k^{(1)})\Omega_2(E_{\text{tot}}, x_{k,\text{tot}})\mathrm{e}^{-\beta(E_1 - X_k x_k^{(1)})}}{Z'(T, X_k)}. \tag{8}$$

By noting that the constant term $\Omega_2(E_{\text{tot}}, x_{k,\text{tot}})$ appears also in $Z'(T, X_k)$, we can finally write eq. (8) as follows

$$P_1(E_1, x_k^{(1)}) = \frac{\Omega_1(E_1, x_k^{(1)})\mathrm{e}^{-\beta(E_1 - X_k x_k^{(1)})}}{Z(T, X_k)}, \tag{9}$$

where

$$Z(T, X_k) = \int \mathrm{d}E_1\, \mathrm{d}x_k^{(1)} \Omega_1(E_1, x_k^{(1)})\mathrm{e}^{-\beta(E_1 - X_k x_k^{(1)})}. \tag{10}$$

Finally, the generalised free energy reads

$$F(T, X_k) = -k_B T \ln Z(T, X_k), \tag{11}$$

from which we can obtain the equations of state for the ensemble under consideration.

We have, for example,

$$\langle E_1 \rangle = -\frac{\partial \ln Z(T, X_k)}{\partial \beta} = \frac{\partial \left[\beta F(T, X_k)\right]}{\partial \beta}, \tag{12}$$

$$\left\langle x_k^{(1)} \right\rangle = \frac{\partial \ln Z(T, X_k)}{\partial \beta X_k} = -\frac{\partial \left[\beta F(T, X_k)\right]}{\partial \beta X_k}. \tag{13}$$