Microcanonical ensemble III

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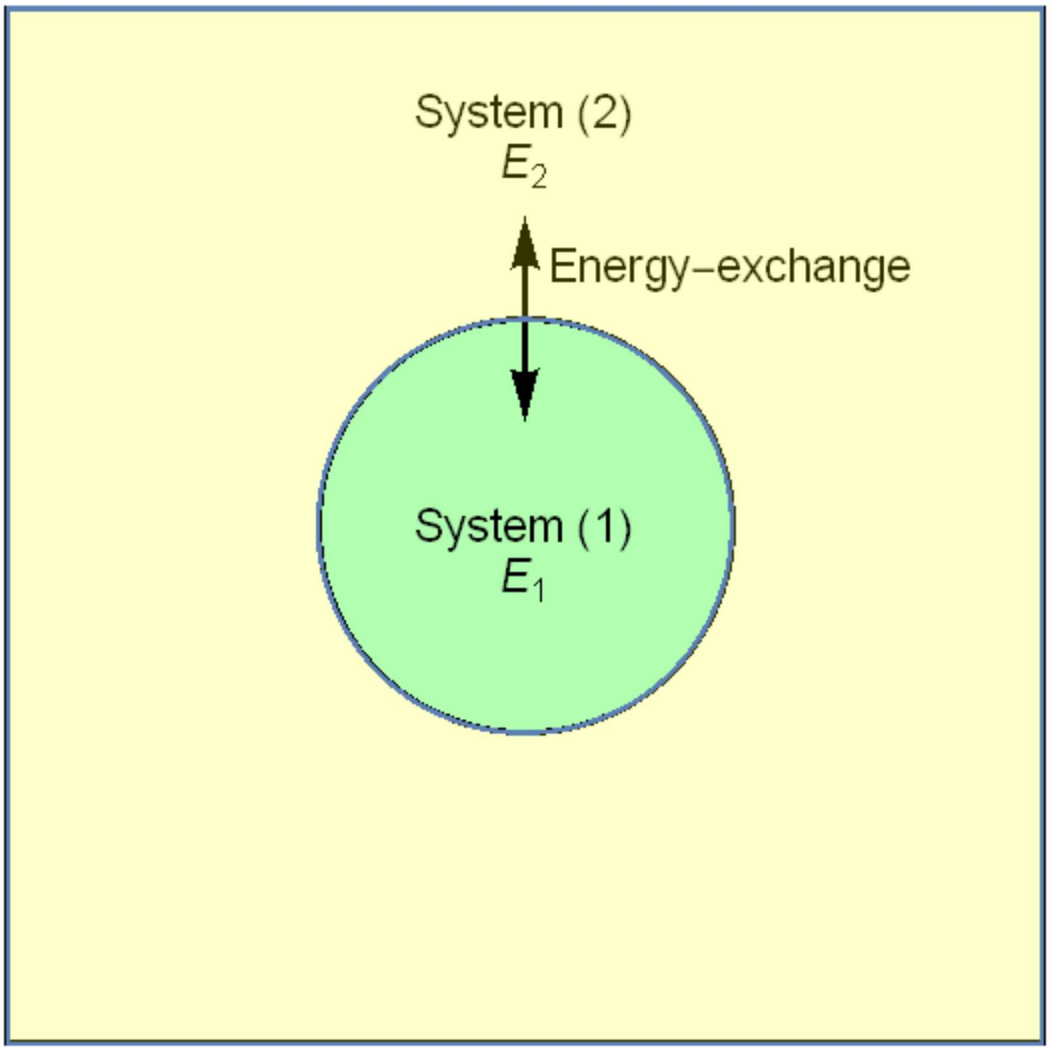
We discuss the microcanonican ensemble in more detail

1. The number of states



The total Hamiltonian consists of the Hamiltonian H_1 for the system 1 (the number of particles N_1) and the Hamiltonian H_2 for the system 2 (the number of particles N_2)

$$H_N = H_{N_1} + H_{N_2}$$

The probability distribution function for the subsystem 1 is obtained as follows. We are not interested in the state of the system 2. So we integrate $f_{MC}({}^{N}\Gamma)$ over all the variables of the system 2. Then we get

$$\begin{aligned}
f_1({}^{N}\Gamma) &= \int d^{N_2}\Gamma f_{MC}({}^{N}\Gamma) \\
&= \int d^{N_2}\Gamma \frac{\delta(E - H_{N_1} - H_{N_2})\delta E}{W(N, E, V, \delta E)} \\
&= \frac{\delta E}{W(N, E, V, \delta E)} \int d^{N_2}\Gamma \delta(E - H_{N_1} - H_{N_2}) \\
&= \frac{\delta E}{W(N, E, V, \delta E)} \Omega_2(N_2, E - H_{N_1}, V)
\end{aligned} \tag{1}$$

where

Γ^{N} is a point of 6N dimensional phase space.

$$f_{MC}({}^{N}\Gamma) = \frac{\delta(E - H_N)\delta E}{W(N, E, V, \delta E)}$$

$$\Omega(N, E, V) = \int d^{N}\Gamma \delta(E - H_N)$$

$$W(N, E, V, \delta E) = \Omega(N, E, V)\delta E$$

We note that the expectation value is defined by

$$\langle A \rangle_{MC} = \int d^{N}\Gamma f_{MC}({}^{N}\Gamma) A({}^{N}\Gamma).$$

Using this definition, we have the expectation value

$$
\begin{aligned}
f_{MC}(E_1) &= \int d^{N_1}\Gamma f_1({}^{N_1}\Gamma)\delta(E_1 - H_{N_1}) \\
&= \frac{\delta E}{W(N,E,V,\delta E)}\int d^{N_1}\Gamma\,\delta(E_1 - H_{N_1})\Omega_2(N_2, E - H_{N_1}, V) \\
&= \frac{\delta E}{W(N,E,V,\delta E)}\Omega_2(N_1, E_1, V)\Omega_2(N_2, E - E_1, V) \\
&= \frac{\delta E}{\Omega(N,E,V,\delta E)\delta E}\Omega_1(N_1, E_1, V)\Omega_2(N_2, E - E_1, V) \\
&= \frac{1}{\Omega(N_{1+2}, E_1 + E_2, V)}\Omega_1(N_1, E_1, V)\Omega_2(N_2, E - E_1, V)
\end{aligned}
$$

Note that

$$
\int_0^E f_{MC}(E_1)dE_1 = 1
$$

since

$$
\begin{aligned}
\Omega_{12}(N,E,V) &= \int d^N\Gamma\,\delta(E - H_{N_1} - H_{N_2}) \\
&= \int_0^E dE_1 \int d^{N_1}\Gamma \int d^{N_2}\Gamma\,\delta(E - E_1 - H_{N_2})\delta(E_1 - H_{N_{11}}) \\
&= \int_0^E dE_1 \int d^{N_1}\Gamma\,\delta(E_1 - H_{N_1}) \int d^{N_2}\Gamma\,\delta(E - E_1 - H_{N_2}) \\
&= \int_0^E dE_1 \Omega_1(N_1, E_1, V)\Omega_2(N_2, E - E_1, V)
\end{aligned}
$$

((**Kubo**))

We consider the two systems (1 and 2). When the energy of the system 1 is between E_1 and $E_1 + dE_1$, while the energy of the system 2 is E_2 and $E_2 + dE_2$, the corresponding number of states is given by

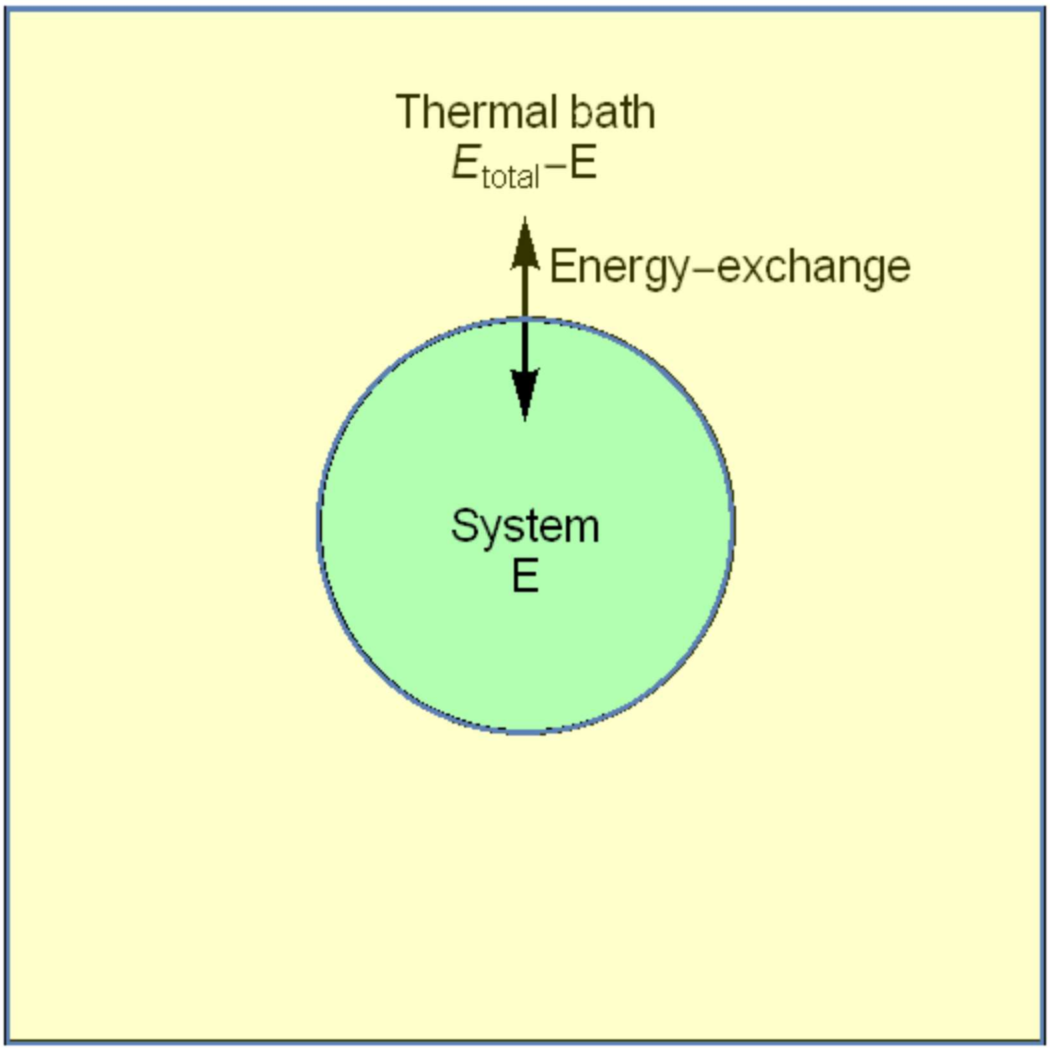
$$
\Omega_1(E_1)\delta E_1 \Omega_2(E_2)\delta E_2
$$

Suppose that $E = E_1 + E_2$. The number of states when the total energy is between E and $E + dE$

$$\int_{E<E1+E2<E+\delta E} \int \Omega_1(E_1)dE_1\Omega_2(E_2)dE_2 = \delta E \int \Omega_1(E_1)dE_1\Omega_2(E-E_1)$$

2. Canonical ensemble

We consider the system (I) surrounded by the thermal bath (II). The total energy is kept constant.



The probability of finding the system between E and $E+\delta E$

$$f(E)\delta E = \frac{\Omega(E)\Omega_{bath}(E_{total}-E)\delta E}{\Omega_{total}(E_{total})}$$

$\Omega_{bath}(E_{total} - E)$ is the density of state for the thermal bath. $\Omega(E)$ is the density of state for the system. $\Omega_{total}(E_{total})$ is the density of states for the combined system (system and thermal). The entropy of the thermal bath is given by

$$k_B \ln \Omega_{bath}(E_{total} - E) = k_B \ln \Omega_{bath}(E_{total}) - k_B[\frac{\partial}{\partial E_{total}} \ln \Omega_{bath}(E_{total})]E + ...$$

$$= S_{bath}(E_{total}) - \frac{\partial S_{bath}(E_{total})}{\partial E_{total}} E + \frac{1}{2!}\frac{\partial^2 S_{bath}(E_{total})}{\partial\ E_{total}} E^2 + ...$$

where

$$k_B \ln \Omega_{bath}(E_{total}) = S_{bath}(E_{total})$$

We define the temperature *T* (in thermal equilibrium) as

$$\frac{\partial S_{bath}(E_{total})}{\partial E_{total}} = \frac{1}{T} = k_B \beta$$

The energy is a function of *T*. So we assume that *T* is an independent variable
Thus we get

$$k_B \ln \Omega_{bath}(E_{total} - E) = S_{bath}(E_{total}) - k_B \beta E$$

or

$$\Omega_{bath}(E_{total} - E) = \exp[\frac{S_{bath}(E_{total})}{k_B} - \beta E] = \exp[\frac{S_{bath}(E_{total})}{k_B}]\exp(-\beta E)$$

The probability is then obtained as

$$f(E)\delta E = \frac{\exp[\frac{S_{bath}(E_{total})}{k_B}]\Omega(E)\exp(-\beta E)\delta E}{\Omega_{total}(E_{total})}$$

or

$$f(E)\delta E = \frac{\exp[\dfrac{S_{bath}(E_{total})}{k_B}]\Omega(E)\exp(-\beta E)\delta E}{\Omega_{total}(E_{total})}$$

or

$$f(E) = \frac{\Omega(E)\exp(-\beta E)}{Z_C(\beta)}$$

where

$$\boxed{Z_C(\beta) = \int_0^\infty \Omega(E)\exp(-\beta E)} \qquad \text{(sum of states, state-sum)}$$

((**Note**))

We consider a function defined by

$$g(E) = k_B \ln[\Omega(E)\Omega_{bath}(E_{bath})] = k_B \ln[\Omega(E)] + k_B \ln[\Omega_{bath}(E_{bath})]$$

with

$$E_{total} = E + E_{bath}$$

Suppose that $g(E)$ has a maximum at $E = E^*$.

$$\begin{aligned}
\frac{dg(E)}{dE} &= k_B[\frac{d\ln\Omega(E)}{dE} + \frac{d\ln\Omega_{bath}(E_{bath})}{dE_{bath}}\frac{dE_{bath}}{dE} \\
&= k_B\frac{d\ln\Omega(E)}{dE} - k_B\frac{d\ln\Omega_{bath}(E_{bath})}{dE_{bath}} \\
&= 0
\end{aligned}$$

or

$$k_B\frac{d\ln\Omega(E)}{dE} - k_B\frac{d\ln\Omega_{bath}(E_{bath})}{dE_{bath}}$$

The left-hand side is related to the system, while the right-hand side is related to the thermal bath. We define the temperature T as

$$k_B \frac{d \ln \Omega_{bath}(E_{bath})}{dE_{bath}} = \frac{\partial S_{bath}}{\partial E_{bath}} = \frac{1}{T}$$

where k_B is the Boltzmann constant. We note that for the condition of local maximum, we need the condition

$$\frac{d^2 g(E)}{dE^2} = k_B \frac{d^2 \ln \Omega(E)}{dE^2} + k_B \frac{d^2 \ln \Omega_{bath}(E_{bath})}{d^2 E_{bath}} < 0$$

or

$$\frac{\partial}{\partial E} \frac{1}{T(E)} + \frac{\partial}{\partial E_{bath}} \frac{1}{T_{bath}(E_{bath})} < 0$$

$$\frac{\partial}{\partial E} T(E) + \frac{\partial}{\partial E_{bath}} T_{bath}(E_{bath}) > 0$$

In general,

$$\frac{\partial}{\partial E_{bath}} T_{bath}(E_{bath}) \to 0 \,,$$

and

$$\frac{\partial}{\partial E} T(E) > 0$$