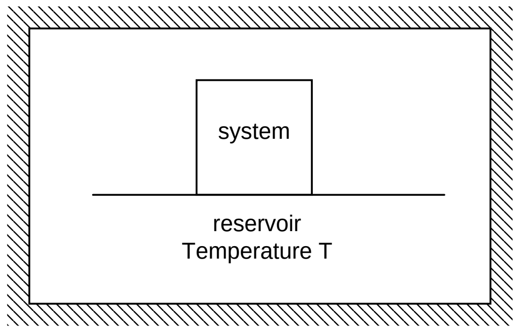
Canonical Ensemble: the Boltzmann Factor

A system that can exchange energy via very weak contact with a temperature bath eventually comes to equilibrium. The *canonical ensemble* describes the statistical distribution in such a system. Why is very weak contact with the reservoir important? Because now the energy E that is *conserved* by the internal dynamics is no longer rigorously fixed as it is in an isolated system—although the coupling with the reservoir is weak, we wait arbitrarily long for the system-reservoir to come to equilibrium. The dynamics of the system remains dominated by the internal interactions, so the probabilities of states are constant on the constant energy surface. But now E may change, and we need to find the energy dependence of the probabilities.



To find the probability distribution over the states of the *system* in the *canonical* ensemble we consider the *combined* system+reservoir as isolated, and described by the *microcanonical* ensemble.

We will calculate the probability P_j of finding the system in a particular microstate j with energy E_j. The probability P_j is proportional to the number of microstates of the *reservoir* consistent with this system microstate, since for the combined system+reservoir each microstate is equally likely. The number of microstates available in the reservoir depends on j through the energy: if the reservoir has energy $E^{(r)}$ when the system is in microstate i it will have energy $E^{(r)} - \Delta E$ with $\Delta E = E_j - E_i$ when the system is n microstate E_j.

Consider the ratio of probabilities for microstates j and i

$$\frac{P_j}{P_i} = \exp\left[\frac{S^{(r)}(E^{(r)} - \Delta E) - S^{(r)}(E^{(r)})}{k_B}\right] \tag{1}$$

(the number of microstates is one for the system multiplied by $\exp(S^{(r)}/k_B T)$ for the reservoir). Since the reservoir is assumed large, ΔE is small compared to $E^{(r)}$ for any system change i to j, and so we can evaluate the quantity inside the exponential as the first term in a Taylor expansion, to find

$$\frac{P_j}{P_i} = \exp\left[-\frac{E_j - E_i}{kT}\right] \tag{2}$$

with T the temperature of the reservoir

$$\frac{1}{T} = \frac{\partial S^{(r)}}{\partial E^{(r)}}. \tag{3}$$

This gives us the result for the probability of system microstate j in the canonical ensemble

$$P_j \propto e^{-\beta E_j} \qquad \text{with} \qquad \beta = \frac{1}{kT}. \tag{4}$$

The proportionality constant is fixed by normalizing the sum of probabilities to unity. It turns out to be useful to focus the calculation on this sum, and we define this as the *canonical partition function* Z

$$Z(T, V, N) = \sum_j e^{-\beta E_j} \tag{5}$$

and then

$$P_j = Z^{-1} e^{-\beta E_j}. \tag{6}$$

Further we define the free energy $F(T, V, N)$

$$F = -kT \ln Z. \tag{7}$$

Note that the probability distribution of the system in contact with the reservoir only depends on the properties of the reservoir through the single parameter T. Also, we have not made use of any argument depending on the *system* being macroscopic, just that the reservoir is very large. The system may in fact be microscopic, even a single state. The temperature T in the expression is the temperature of the reservoir—for a microscopic system its temperature is not well defined from internal quantities, and so it is often *defined* to be that of the reservoir.