SECOND EDITION

Thermal Physics

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In this chapter we develop the principles that permit us to calculate the values of the physical properties of a system as a function of the temperature. We assume that the system $\mathcal{S}$ of interest to us is in thermal equilibrium with a very large system $\mathcal{R}$, called the **reservoir**. The system and the reservoir will have a common temperature τ because they are in thermal contact.

The total system $\mathcal{R} + \mathcal{S}$ is a closed system, insulated from all external influences, as in Figure 3.1. The total energy $U_0 = U_{\mathcal{R}} + U_{\mathcal{S}}$ is constant. In particular, if the system is in a state of energy ε_s, then $U_0 - \varepsilon_s$ is the energy of the reservoir.

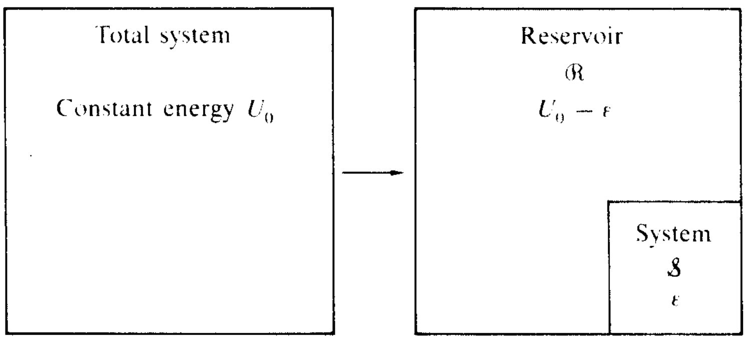


Figure 3.1 Representation of a closed total system decomposed into a reservoir $\mathcal{R}$ in thermal contact with a system $\mathcal{S}$.

BOLTZMANN FACTOR

A central problem of thermal physics is to find the probability that the system $\mathcal{S}$ will be in a specific quantum state s of energy ε_s. This probability is proportional to the Boltzmann factor.

When we specify that should be in the state s, the number of accessible states of the total system is reduced to the number of accessible states of the reservoir $\mathcal{R}$, at the appropriate energy. That is, the number $g_{\mathcal{R}+\mathcal{S}}$ of states

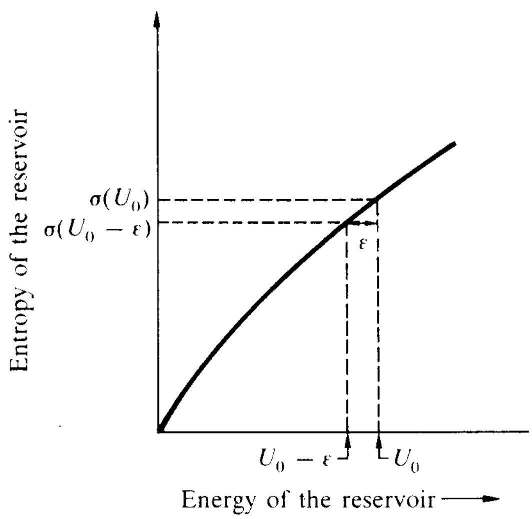


Figure 3.2 The change of entropy when the reservoir transfers energy ε to the system. The fractional effect of the transfer on the reservoir is small when the reservoir is large, because a large reservoir will have a high entropy.

accessible to $\mathcal{R} + \mathcal{S}$ is

$$g_{\mathcal{R}} \times 1 = g_{\mathcal{R}} , \tag{1}$$

because for our present purposes we have specified the state of $\mathcal{S}$.

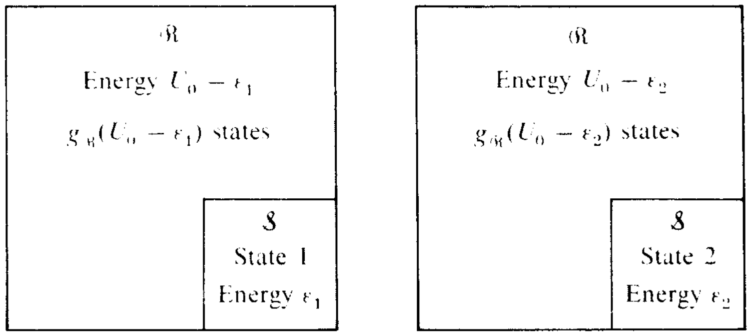
If the system energy is ε_s, the reservoir energy is $U_0 - \varepsilon_s$. The number of states accessible to the reservoir in this condition is $g_{\mathcal{R}}(U_0 - \varepsilon_s)$, as in Figure 3.2. The ratio of the probability that the system is in quantum state 1 at energy ε_1 to the probability that the system is in quantum state 2 at energy ε_2 is the ratio of the two multiplicities:

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\text{Multiplicity of } \mathcal{R} \text{ at energy } U_0 - \varepsilon_1}{\text{Multiplicity of } \mathcal{R} \text{ at energy } U_0 - \varepsilon_2} = \frac{g_{\mathcal{R}}(U_0 - \varepsilon_1)}{g_{\mathcal{R}}(U_0 - \varepsilon_2)} . \tag{2}$$

This result is a direct consequence of what we have called the fundamental assumption. The two situations are shown in Figure 3.3. Although questions about the system depend on the constitution of the reservoir, we shall see that the dependence is only on the temperature of the reservoir.

If the reservoirs are very large, the multiplicities are very, very large numbers. We write (2) in terms of the entropy of the reservoir:

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp[\sigma_{\mathcal{R}}(U_0 - \varepsilon_1)]}{\exp[\sigma_{\mathcal{R}}(U_0 - \varepsilon_2)]} = \exp[\sigma_{\mathcal{R}}(U_0 - \varepsilon_1) - \sigma_{\mathcal{R}}(U_0 - \varepsilon_2)] . \tag{3}$$



(a) (b)

Figure 3.3 The system in (a), (b) is in quantum state 1, 2. The reservoir has $g_{\Re}(U_0 - \varepsilon_1)$, $g_{\Re}(U_0 - \varepsilon_2)$ accessible quantum states, in (a) and (b) respectively.

With

$$\Delta\sigma_{\Re} \equiv \sigma_{\Re}(U_0 - \varepsilon_1) - \sigma_{\Re}(U_0 - \varepsilon_2) \ , \tag{4}$$

the probability ratio for the two states 1, 2 of the system is simply

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \exp(\Delta\sigma_{\Re}). \tag{5}$$

Let us expand the entropies in (4) in a Taylor series expansion about $\sigma_{\Re}(U_0)$. The Taylor series expansion of $f(x)$ about $f(x_0)$ is

$$f(x_0 + a) = f(x_0) + a\left(\frac{df}{dx}\right)_{x=x_0} + \frac{1}{2!}a^2\left(\frac{d^2f}{dx^2}\right)_{x=x_0} + \cdots . \tag{6}$$

Thus

$$\begin{aligned} \sigma_{\Re}(U_0 - \varepsilon) &= \sigma_{\Re}(U_0) - \varepsilon(\partial\sigma_{\Re}/\partial U)_{V,N} + \cdots \\ &= \sigma_{\Re}(U_0) - \varepsilon/\tau + \cdots , \end{aligned} \tag{7}$$

where $1/\tau \equiv (\partial\sigma_{\Re}/\partial U)_{V,N}$ gives the temperature. The partial derivative is taken at energy U_0. The higher order terms in the expansion vanish in the limit of an infinitely large reservoir.*

Therefore $\Delta\sigma_{\mathcal{R}}$ defined by (4) becomes

$$\Delta\sigma_{\mathcal{R}} = -(\varepsilon_1 - \varepsilon_2)/\tau. \tag{8}$$

The final result of (5) and (8) is

$$\boxed{\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp(-\varepsilon_1/\tau)}{\exp(-\varepsilon_2/\tau)}.} \tag{9}$$

A term of the form $\exp(-\varepsilon/\tau)$ is known as a **Boltzmann factor**. This result is of vast utility. It gives the ratio of the probability of finding the system in a single quantum state 1 to the probability of finding the system in a single quantum state 2.

Partition Function

It is helpful to consider the function

$$Z(\tau) = \sum_s \exp(-\varepsilon_s/\tau) \ , \tag{10}$$

called the **partition function**. The summation is over the Boltzmann factor $\exp(-\varepsilon_s/\tau)$ for all states s of the system. The partition function is the proportionality factor between the probability $P(\varepsilon_s)$ and the Boltzmann factor $\exp(-\varepsilon_s/\tau)$:

$$P(\varepsilon_s) = \frac{\exp(-\varepsilon_s/\tau)}{Z}. \tag{11}$$

We see that $\sum P(\varepsilon_s) = Z/Z = 1$: the sum of all probabilities is unity.

The result (11) is one of the most useful results of statistical physics. The average energy of the system is $U = \langle\varepsilon\rangle = \sum \varepsilon_s P(\varepsilon_s)$, or

$$U = \frac{\sum \varepsilon_s \exp(-\varepsilon_s/\tau)}{Z} = \tau^2(\partial \log Z/\partial\tau). \tag{12}$$

* We expand $\sigma(U_0 - \varepsilon)$ and not $g(U_0 - \varepsilon)$ because the expansion of the latter quantity immediately gives convergence difficulties.