

Fig. 4.2 The system of interest A is held at a constant temperature T by exchanging energy with the surroundings B. The composite system AB is isolated from the rest of the universe by means of an adiabatic, rigid, and impermeable wall.

Similarly, various statistical ensembles can be derived from the microcanonical ensemble. For this reason, the microcanonical ensemble is important conceptually despite the computational awkwardness you saw in Exercise 4.3.

4.5.1 Closed System Held at a Constant Temperature

Let us take a closed system A held at a constant temperature T . The number of particles N in A and the volume of A are both constant. But the system is allowed to exchange energy with the surroundings, which is assumed to be macroscopic. As we saw in Sect. 2.13.1, this thermal contact is what maintains the temperature of the system at a desired value.

Due to the energy exchange with the surroundings, the energy E_a of A fluctuates over time. Our immediate goal is to find the probability $p(E_a)dE_a$ that the energy of A lies somewhere in the interval $(E_a - dE_a, E_a]$. We use microcanonical ensemble for this purpose.

As we have indicated already, a microcanonical ensemble is suitable for describing an isolated system, which system A is not. In order to make the microcanonical ensemble applicable to the current situation, we construct a composite system AB consisting of A and the macroscopic surroundings B, and then isolate AB from the rest of the universe by means of an adiabatic, rigid, and impermeable wall as shown in Fig. 4.2. We shall assume that the interaction between A and B is sufficiently weak in the sense that

$$H_{ab} \approx H_a + H_b . \quad (4.57)$$

Because the composite system AB is isolated, the microcanonical ensemble applies. As in (4.16), we have

$$E_{ab} - \Delta E < H_{ab} \leq E_{ab} \quad (4.58)$$

for the allowed values of H_{ab} .

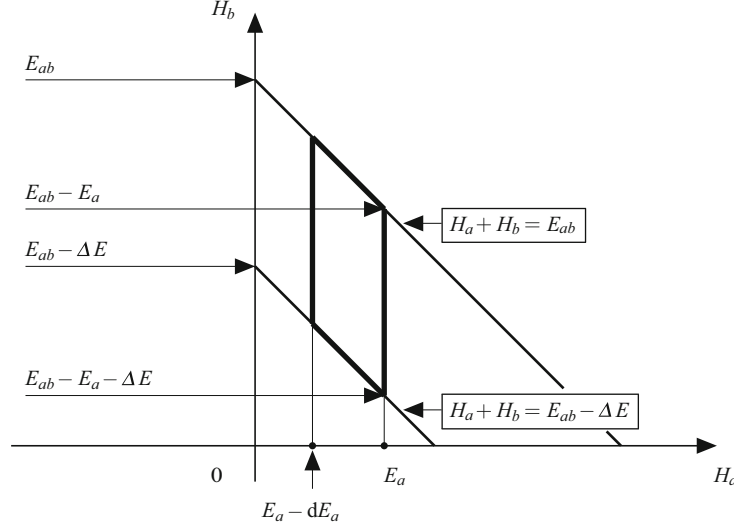


Fig. 4.3 The parallelogram region defined by four lines $H_a + H_b = E_{ab}$, $H_a + H_b = E_{ab} - \Delta E$, $H_a = E_a$, and $H_a = E_a - dE_a$ contains all the microstates accessible to the composite system AB that are consistent with (4.58) and (4.59).

We recall that all the microstates of AB consistent with this condition on H_{ab} are equally probable. Thus, to compute $p(E_a)dE_a$, we need to figure out the total number of microstates of AB that are consistent with both (4.58) and the condition

$$E_a - dE_a < H_a \leq E_a . \quad (4.59)$$

The desired probability is this number divided by the total number of microstates of AB, which is simply $\overline{\Omega}_{ab}(E_{ab})\Delta E$.

Now, the number of microstates accessible to A under the condition (4.59) is simply

$$\overline{\Omega}_a(E_a)dE_a , \quad (4.60)$$

where we suppressed the dependence of $\overline{\Omega}_a$ on the system volume and the number of mechanical degrees of freedom of the system as they are constant in this case. But, when A is at a particular microstate with a given energy, B can still be in various different microstates that are consistent with the remaining energy left to it.

As seen in Fig. 4.3, the conditions (4.58) and (4.59) specify the allowed values of H_b . The figure indicates that the interval for H_b depends on the exact value of H_a . This leads to a complication in figuring out the number of microstates accessible to system B. However, for sufficiently small dE_a , we may replace the parallelogram indicated by thick solid lines by the rectangle defined by $H_a = E_a$, $H_a = E_a - dE_a$, $H_b = E_{ab} - E_a$, and $H_b = E_{ab} - E_a - \Delta E$. Thus, we may write

$$E_{ab} - E_a - \Delta E < H_b \leq E_{ab} - E_a . \quad (4.61)$$

Accordingly, the number of microstates accessible to B that are consistent with both the conditions (4.58) and (4.59) is given by

$$\overline{\Omega}_b(E_{ab} - E_a)\Delta E . \quad (4.62)$$

The total number of microstates accessible to the composite system AB as a whole is then the product of (4.60) and (4.62):

$$\overline{\Omega}_a(E_a)dE_a\overline{\Omega}_b(E_{ab} - E_a)\Delta E . \quad (4.63)$$

So, the desired probability is

$$p(E_a)dE_a = \frac{\overline{\Omega}_b(E_{ab} - E_a)\Delta E\overline{\Omega}_a(E_a)dE_a}{\overline{\Omega}_{ab}(E_{ab})\Delta E} . \quad (4.64)$$

The normalization condition of $p(E_a)$ leads to

$$\overline{\Omega}_{ab}(E_{ab})\Delta E = \int \overline{\Omega}_b(E_{ab} - E_a)\Delta E\overline{\Omega}_a(E_a)dE_a , \quad (4.65)$$

where the integration is with respect to all possible values of E_a . This result is quite natural. In order to find out the total number of microstates accessible to AB, we first figure out the number of microstates accessible to AB when H_a is within a certain interval indicated by (4.59). This gives (4.63). Once the number of microstates is obtained for all the other intervals of width dE_a , we can simply add up the results to obtain the total number of microstates.

4.5.2 Canonical Distribution

As it is, (4.64) is not very useful for practical computations. As we saw in Exercise 4.3, $\overline{\Omega}$ is a very awkward function to work with. To transform (4.64) a bit further, we recall Boltzmann's entropy formula (4.26) and write

$$\overline{\Omega}_b(E_{ab} - E_a)\Delta E = e^{\ln\overline{\Omega}_b(E_{ab} - E_a)\Delta E} = e^{S_b(E_{ab} - E_a)/k_B} . \quad (4.66)$$

Expanding $S_b(E_{ab} - E_a)$ in a Taylor series, we find

$$S_b(E_{ab} - E_a) = S_{b0} - \left. \frac{\partial S_b(E_b)}{\partial E_b} \right|_0 E_a + \text{h.o.} = S_{b0} - \frac{E_a}{T} + \text{h.o.} , \quad (4.67)$$

where the subscript 0 on S_b and its derivative indicates that they are to be computed under the condition that $E_b = E_{ab}$, while T defined in the last step is the temperature of the surroundings B when its energy is E_{ab} .

At this point, we note that the surroundings B can be chosen arbitrarily large compared to A, and hence the numbers of mechanical degrees of freedom of these two systems can be made to satisfy $f_a \ll f_b$. This implies that $E_{ab} \gg E_a$ for all

reasonable values of E_a and hence T is quite insensitive to the exact value of E_a . This being the case, T can be referred to as the temperature of B regardless of the exact value of E_a and we can safely ignore the higher order terms in the Taylor series expansion of S_b .²²

Recalling that $\beta := 1/k_B T$, we can rewrite (4.66) as

$$\overline{\Omega}_b(E_{ab} - E_a)\Delta E = e^{S_{b0}/k_B} e^{-\beta E_a}, \quad (4.68)$$

in terms of which (4.64) and (4.65) become

$$p(E_a)dE_a = \frac{e^{S_{b0}/k_B} e^{-\beta E_a} \overline{\Omega}_a(E_a)dE_a}{\overline{\Omega}_{ab}(E_{ab})\Delta E} \quad (4.69)$$

and

$$\overline{\Omega}_{ab}(E_{ab})\Delta E = e^{S_{b0}/k_B} \int \overline{\Omega}_a(E_a) e^{-\beta E_a} dE_a, \quad (4.70)$$

respectively.

In what follows, we will be concerned only with system A. Thus, we drop the subscript a without a risk of confusion. Combining the last two equations,

$$p(E)dE = \frac{1}{Z} \overline{\Omega}(E) e^{-\beta E} dE, \quad (4.71)$$

in which

$$Z := \int \overline{\Omega}(E) e^{-\beta E} dE \quad (4.72)$$

is the **canonical partition function**.²³ In Sect. 4.5.3, we see that (4.72) agrees with (3.162).

The free energy associated with this ensemble, by definition, is the **Helmholtz free energy**:

$$F = -k_B T \ln Z. \quad (4.73)$$

This definition, along with (2.172), leads to Gibbs's entropy formula as you will see in Exercise 4.5. Note that $\overline{\Omega}$ is a function of E , the volume V , and the number of mechanical degrees of freedom f of the system. When it is multiplied by the Boltzmann factor and integrated with respect to E , the final answer Z and hence F will be functions of T , V , and f . That is, (4.73) is a fundamental equation of the system.

We recall that $\overline{\Omega}(E)$ is the density of states. So, $\overline{\Omega}(E)dE$ is the number of microstates of system A within the interval $(E - dE, E]$. We already remarked that each of these microstates are equally probable.²⁴ Accordingly, (4.71) has the following interpretation. The factor $e^{-\beta E}/Z$ is the probability that the system A is at a *particular* microstate with energy somewhere in the interval $(E - dE, E]$. But, there are $\overline{\Omega}(E)dE$ equally probable microstates within this interval. Therefore, the probability that the energy of system A is in the interval $(E - dE, E]$, irrespective of which particular microstate it is in, is given by (4.71).