

# Chapter 10

## Entropy III

### 10.1 The law of increase of entropy

Recall that the entropy is defined by [Eqs. (8.24) and (6.19)]

$$S = k \ln V(E) \approx k \ln \Omega(E) \approx k\beta E + k \ln Z, \quad (10.1)$$

where each approximation is subject to approximately  $1/N$  corrections. Previously the last form was derived from the canonical distribution, but it follows now immediately from Eq. (9.68):

$$\Omega(E) \sim e^{\beta E} \chi(\beta) \frac{1}{\sqrt{2\pi(\ln \chi)''(\beta)}}, \quad (10.2)$$

so

$$\ln \Omega(E) = \beta E + \ln \chi(\beta) - \frac{1}{2} \ln[2\pi(\ln \chi)''(\beta)]. \quad (10.3)$$

But  $\ln \chi = O(N)$ , hence  $\ln[2\pi(\ln \chi)''] = O(\ln N)$ , so the last term in Eq. (10.3) is negligible for large  $N$ . Thus the three forms in Eq. (10.1) are all equivalent as  $N \rightarrow \infty$ . We will here use the third form, since it is exactly additive: If  $H = H_1 + H_2$  represents two noninteracting subsystems,  $E = E_1 + E_2$ ,  $Z = Z_1 Z_2$ , and

$$S = k(\beta E + \ln Z) = k(\beta E_1 + \ln Z_1) + k(\beta E_2 + \ln Z_2) = S_1 + S_2. \quad (10.4)$$

This assumes that the two systems are in thermal equilibrium (have a common temperature  $T = 1/k\beta$ ) and are *non-interacting*.

Suppose we now have two systems at different temperatures. Suppose system 1 has inverse temperature  $\beta_1$ , and system 2 has inverse temperature  $\beta_2$ . Let's put the two systems into contact with each other, but *isolated* from the outside world. The weak interactions between the two systems eventually result in bringing them into equilibrium, at an inverse temperature  $\beta$ . Before the two systems are in contact, the entropies are

$$\frac{S_{1i}}{k} = \beta_1 U_{1i} + \ln Z_1(\beta_1), \quad \frac{S_{2i}}{k} = \beta_2 U_{2i} + \ln Z_2(\beta_2), \quad (10.5)$$

and the entropy of the whole is  $S = S_{1i} + S_{2i}$ . Here, we've used the thermodynamic notation of  $U$  in place of  $E$ , and the energies are given by the saddle point condition (or the equivalent canonical relation)

$$U_{1i} = -(\ln Z_1)'(\beta_1), \quad U_{2i} = -(\ln Z_2)'(\beta_2). \quad (10.6)$$

Because energy is conserved, after the systems are brought together and reach equilibrium, the energy is  $U = U_{1i} + U_{2i}$ , and the entropy is

$$\begin{aligned} \frac{S_f}{k} &= \beta(U_{1i} + U_{2i}) + \ln Z_1(\beta)Z_2(\beta) \\ &= -\beta[(\ln Z_1)'(\beta_1) + (\ln Z_2)'(\beta_2)] + \ln Z_1(\beta) + \ln Z_2(\beta). \end{aligned} \quad (10.7)$$

The change in the entropy is

$$\begin{aligned} \frac{S_f - S_i}{k} &= (\beta_1 - \beta)(\ln Z_1)'(\beta_1) + (\beta_2 - \beta)(\ln Z_2)'(\beta_2) + \ln \frac{Z_1(\beta)Z_2(\beta)}{Z_1(\beta_1)Z_2(\beta_2)} \\ &= F_1(\beta_1, \beta) + F_2(\beta_2, \beta), \end{aligned} \quad (10.8)$$

where

$$F_j(\beta_j, \beta) = (\beta_j - \beta)(\ln Z_j)'(\beta_j) + \ln \frac{Z_j(\beta)}{Z_j(\beta_j)}. \quad (10.9)$$

Notice that, first,

$$F_j(\beta_j, \beta_j) = 0. \quad (10.10)$$

Next,

$$\frac{\partial F_j}{\partial \beta}(\beta_j, \beta) = -(\ln Z_j)'(\beta_j) + (\ln Z_j)'(\beta), \quad (10.11)$$

so further

$$\frac{\partial F}{\partial \beta}(\beta_j, \beta_j) = 0. \quad (10.12)$$

Finally, from Eq. (6.51) or (9.63),

$$\frac{\partial^2 F}{\partial \beta^2}(\beta_j, \beta) = (\ln Z_j)''(\beta) = \langle (H - \langle H \rangle)^2 \rangle > 0, \quad (10.13)$$

so considered as a function of  $\beta$ ,  $F_j(\beta_j, \beta)$  has a minimum at  $\beta = \beta_j$  (where it vanishes) and is otherwise positive. This proves that

$$S_f \geq S_i, \quad (10.14)$$

where equality only occurs if  $\beta_1 = \beta_2 = \beta$ , that is, the two systems are originally at the same temperature. If they are not, the entropy of the whole system always increases. This is a general statement of the second law of thermodynamics.

## 10.2 Concept of entropy

Let's revisit the concept of entropy based on our new appreciation of  $\beta$  as a saddle point. Recall, as we defined in Eq. (8.18),

$$S = k \ln V(E, a), \quad (10.15)$$

where  $a$  stands for some parameter characterizing the system, such as the size of the box it is contained in. The volume of phase space with energy  $H \leq E$  is

$$V(E, a) = \int_0^E dE' \Omega(E', a), \quad (10.16)$$

according to Eq. (3.19). The structure function  $\Omega(E', a)$  is such a rapidly increasing function of  $E'$  that only the values of  $E'$  near  $E$  are significant. Recall from (9.86) that if we choose a path not passing through the saddle point, for which

$$(\ln \chi)'(\beta) = -E, \quad (10.17)$$

but through a slightly different point  $\bar{\beta}$ ,

$$\Omega(E) \sim \frac{e^{\bar{\beta}E} \chi(\bar{\beta})}{\sqrt{2\pi(\ln \chi)''(\bar{\beta})}} e^{-[E+(\ln \chi)'(\bar{\beta})]^2/2(\ln \chi)''(\bar{\beta})}, \quad (10.18)$$

so if we now substitute  $E \rightarrow E'$ ,  $\bar{\beta} \rightarrow \beta$ , and call  $(\ln \chi)'(\beta) = -E$ , we have

$$\Omega(E') \sim \frac{e^{\beta E'} \chi(\beta)}{\sqrt{2\pi(\ln \chi)''(\beta)}} e^{-(E'-E)^2/2(\ln \chi)''(\beta)}. \quad (10.19)$$

Inserting this into Eq. (10.16), we get

$$V(E) = \frac{e^{\beta E} \chi(\beta)}{\sqrt{2\pi(\ln \chi)''(\beta)}} \int_0^E dE' e^{\beta(E'-E)-(E'-E)^2/2(\ln \chi)''(\beta)}. \quad (10.20)$$

Writing the integral here in terms of  $x = (E - E')/E$ ,

$$E \int_0^1 dx e^{-\beta E x} e^{-E^2 x^2/2(\ln \chi)''(\beta)}, \quad (10.21)$$

we see that because  $\beta E \sim N$ , the first exponential is vanishingly small unless  $x \sim 1/N$ , but because  $(\ln \chi)''(\beta) \sim E/\beta \sim E^2/N$ , the second exponent is nearly unity then. So we can drop the Gaussian (quadratic) term, and the integral is

$$E \int_0^1 dx e^{-\beta E x} = \frac{1}{\beta} (1 - e^{-\beta E}) \sim \frac{1}{\beta}, \quad (10.22)$$

and

$$V(E) = \frac{e^{\beta E} \chi(\beta)}{\beta \sqrt{2\pi(\ln \chi)''(\beta)}} = \frac{\Omega(\beta)}{\beta}, \quad (10.23)$$

up to  $1/N$  corrections for a system with  $N$  subsystems. This agrees with the result found more heuristically in Eq. (8.22).

Thus, once again we write

$$S = k \ln V = k \ln \Omega = k[\beta E + \ln \chi(\beta)], \quad (10.24)$$

always dropping terms not of  $O(N)$ . Thermodynamically we should have from Eq. (8.15)

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_a. \quad (10.25)$$

To verify this from the third form in Eq. (10.24) we must be careful, because  $\beta$  depends on  $E$  through the saddle point condition:

$$\left( \frac{\partial S}{\partial E} \right)_a = k \left[ \beta + E \left( \frac{\partial \beta}{\partial E} \right)_a + (\ln \chi)'(\beta) \left( \frac{\partial \beta}{\partial E} \right)_a \right] = k\beta = \frac{1}{T}, \quad (10.26)$$

where we used the saddle point condition (10.17).

Recall further we had the following formula for the “average force,” Eq. (8.4),

$$\begin{aligned} \bar{\mathcal{F}}_a &= -\left\langle \frac{\partial H}{\partial a} \right\rangle = \frac{1}{\Omega(E, a)} \frac{\partial}{\partial a} V(E, a) \\ &= \frac{1}{\beta V(E, a)} \frac{\partial}{\partial a} V(E, a) = kT \frac{\partial}{\partial a} \ln V(E, a) \\ &= T \left( \frac{\partial S}{\partial a} \right)_E, \end{aligned} \quad (10.27)$$

which is the second equation in Eq. (8.15). Now using the last form in Eq. (10.24), and noting again that  $\ln V$  is stationary with respect to  $\beta$  variations,

$$\bar{\mathcal{F}}_a = kT \frac{\partial}{\partial a} [\beta E + \ln \chi(\beta)] = kT \frac{\partial}{\partial a} \ln \chi \Big|_{\beta}, \quad (10.28)$$

or in terms of the Helmholtz free energy given by Eqs. (6.21) and (6.22)

$$F = -kT \ln \chi(\beta) = U - TS, \quad (10.29)$$

$$\bar{\mathcal{F}}_a = - \left( \frac{\partial F}{\partial a} \right)_T, \quad (10.30)$$

which generalizes Eq. (6.29).

We might finally remark that  $F$  measures the ability of the system to do work while *maintaining constant temperature*, in contact with a heat bath:

$$\delta W = -dU + \delta Q, \quad (10.31)$$

so

$$\begin{aligned} W &= \int_1^2 \delta W = U_1 - U_2 + \int_1^2 \delta Q = U_1 - U_2 + \int_1^2 T dS \\ &= U_1 - U_2 + T(S_2 - S_1) = F_1 - F_2. \end{aligned} \quad (10.32)$$

The generalization of Eqs. (6.26) and (6.27) are

$$\begin{aligned} dF &= dU - d(TS) = T dS - \bar{\mathcal{F}}_1 da - d(TS) \\ &= -S dT - \bar{\mathcal{F}}_a da, \end{aligned} \quad (10.33)$$

and

$$S = - \left( \frac{\partial F}{\partial T} \right)_a, \quad \bar{\mathcal{F}}_a = - \left( \frac{\partial F}{\partial a} \right)_T. \quad (10.34)$$

The final consistency check consists in verifying the formula for the internal energy:

$$\begin{aligned} U &= F + TS = F - T \left( \frac{\partial F}{\partial T} \right)_a = -T^2 \left( \frac{\partial}{\partial T} \frac{F}{T} \right)_a \\ &= kT^2 \left( \frac{\partial}{\partial T} \ln \chi \right)_a = kT^2 \frac{\partial \beta}{\partial T} \left( \frac{\partial}{\partial \beta} \ln \chi \right)_a = - \frac{\partial}{\partial \beta} \ln \chi(\beta, a), \end{aligned} \quad (10.35)$$

which is Eq. (10.17).