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)]

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

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):

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

so

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

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 $N \to \infty$. 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

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

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 β_1, and system 2 has inverse temperature β_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 β. Before the two systems are in contact, the entropies are

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

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)

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

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

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

The change in the entropy is

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

where

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

Notice that, first,

$$F_j(\beta_j, \beta_j) = 0. \tag{10.10}$$

Next,

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

so further

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

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

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

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

$$S_f \geq S_i, \tag{10.14}$$

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 β as a saddle point. Recall, as we defined in Eq. (8.18),

$$S = k \ln V(E, a), \tag{10.15}$$

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

$$V(E, a) = \int_0^E dE' \, \Omega(E', a), \tag{10.16}$$

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

$$(\ln \chi)'(\beta) = -E, \tag{10.17}$$

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

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

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

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

Inserting this into Eq. (10.16), we get

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

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

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

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

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

and

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

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

Thus, once again we write

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

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

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

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

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

where we used the saddle point condition (10.17).

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

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

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 β variations,

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

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

$$F = -kT \ln \chi(\beta) = U - TS, \tag{10.29}$$

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

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:

$$\delta W = -dU + \delta Q, \tag{10.31}$$

so

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

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

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

and

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

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

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

which is Eq. (10.17).