

Chapter 13

Entropy V

Quantum mechanically, we could define the entropy as

$$S = k \ln N(E, a), \quad (13.1)$$

where $N(E, a)$ is the number of states with energy $\leq E$. That is, from Eq. (11.5),

$$N(E, a) = \sum_{E_l \leq E} g_l = \int_0^E dE' \Omega(E', a), \quad (13.2)$$

or

$$\frac{\partial}{\partial E} N(E, a) = \Omega(E, a). \quad (13.3)$$

If we define a projection operator by [analogous to the characteristic function (8.2)]

$$\begin{aligned} \psi_E(H) &= \int_0^E dE' \delta(E' - H) \\ &= \int_0^E dE' \sum_{l,k} |E_l, k\rangle \delta(E' - E_l) \langle E_l, k| \\ &= \sum_{E_l \leq E, k} |E_l, k\rangle \langle E_l, k|, \end{aligned} \quad (13.4)$$

the trace of which is

$$\text{Tr } \psi_E(H) = N(E, a). \quad (13.5)$$

As before, we need to define smoothed quantities:

$$\epsilon N_\epsilon(E, a) = \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \text{Tr } \psi_{E'}(H), \quad (13.6)$$

so, according to Eq. (11.17),

$$\epsilon \frac{d}{dE} N_\epsilon(E, a) = \text{Tr } \psi_{E+\epsilon/2}(H) - \text{Tr } \psi_{E-\epsilon/2}(H) = \Omega_\epsilon(E, a), \quad (13.7)$$

which is the number of states between $E - \epsilon/2$ and $E + \epsilon/2$. This is equivalent to

$$N_\epsilon(E, a) = \frac{1}{\epsilon} \int_0^E dE' \Omega_\epsilon(E', a) \sim \frac{\Omega_\epsilon(E, a)}{\epsilon\beta}, \quad (13.8)$$

since only a small region of width $kT = 1/\beta$ makes a significant contribution to the integral. [The situation is precisely analogous to the classical discussion culminating in Eq. (10.23).] So again we find

$$S = k \ln N_\epsilon(E, a) = k \ln \Omega_\epsilon(E, a)/\epsilon = k[\beta E + \ln \chi(\beta)], \quad (13.9)$$

according to Eq. (11.30).

What about the force? Using Eq. (11.16), we find

$$\langle \mathcal{F}_a \rangle = -\left\langle \frac{\partial H}{\partial a} \right\rangle = -\frac{1}{\Omega_\epsilon(E)} \text{Tr} \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \delta(E' - H) \frac{\partial H}{\partial a}. \quad (13.10)$$

Now from Eq. (13.4)

$$\begin{aligned} \frac{\partial}{\partial a} \text{Tr} \psi_E(H) &= -\int_0^E dE' \text{Tr} \left[\frac{d}{dE'} \left(\delta(E' - H) \frac{\partial H}{\partial a} \right) \right] \\ &= -\text{Tr} \delta(E - H) \frac{\partial H}{\partial a}, \end{aligned} \quad (13.11)$$

since $\delta(-H) = 0$ if $H > 0$. There is no ordering ambiguity here because of the property of the trace: $\text{Tr} AB = \text{Tr} BA$. Therefore, from Eqs. (13.6) and (13.8)

$$\begin{aligned} \langle \mathcal{F}_a \rangle &= \frac{1}{\Omega(E, a)} \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \frac{\partial}{\partial a} \text{Tr} \psi_{E'}(H) \\ &= \frac{\epsilon}{\Omega_\epsilon(E)} \frac{\partial}{\partial a} N_\epsilon(E, a) \\ &= kT \frac{\partial}{\partial a} \ln N_\epsilon(E, a) = T \left(\frac{\partial S}{\partial a} \right)_E \\ &= kT \left(\frac{\partial}{\partial a} \ln \chi(\beta, a) \right)_\beta. \end{aligned} \quad (13.12)$$

Note that this is completely analogous to Eqs. (10.27) and (10.28). The last step uses the property that $\ln N_\epsilon$ is stationary with respect to β variations, just as in Eq. (10.28).

We have, then

$$\begin{aligned} dN_\epsilon(E, a) &= \frac{\partial N_\epsilon}{\partial E} dE + \frac{\partial N_\epsilon}{\partial a} da \\ &= \frac{\Omega_\epsilon}{\epsilon} dE + \frac{\Omega_\epsilon}{\epsilon} \langle \mathcal{F}_a \rangle da, \end{aligned} \quad (13.13)$$

or

$$\frac{dN_\epsilon}{\Omega_\epsilon/\epsilon} = dE + \langle \mathcal{F}_a \rangle da, \quad (13.14)$$

or

$$\frac{1}{\beta} \frac{dN_\epsilon}{N_\epsilon} = dE + \langle \mathcal{F}_a \rangle da, \quad (13.15)$$

or

$$T dS = dU + \langle \mathcal{F}_a \rangle da, \quad (13.16)$$

which is the first law of thermodynamics, once again.

Of course, these results may be immediately obtained from the canonical distribution. For example,

$$\begin{aligned} \langle \mathcal{F}_a \rangle &= -\left\langle \frac{\partial H}{\partial a} \right\rangle = -\frac{1}{\chi(\beta)} \text{Tr} \left(e^{-\beta H} \frac{\partial H}{\partial a} \right) \\ &= \frac{1}{\beta} \frac{1}{\chi(\beta)} \frac{\partial}{\partial a} \text{Tr} e^{-\beta H} = \frac{1}{\beta} \frac{\partial}{\partial a} \ln \chi. \end{aligned} \quad (13.17)$$

We further recall from Eq. (6.7)

$$\begin{aligned} \frac{S}{k} &= -\text{Tr} \rho \ln \rho = -\text{Tr} \rho \ln \left(\frac{e^{-\beta H}}{\chi} \right) \\ &= \beta \text{Tr} \rho H + \ln \chi = \beta \langle H \rangle + \ln \chi \\ &= \beta U + \ln \chi, \end{aligned} \quad (13.18)$$

or

$$S = \frac{1}{T} (U - F), \quad (13.19)$$

recalling that the Helmholtz free energy is $F = -kT \ln \chi$.