Chapter 13

Entropy V

Quantum mechanically, we could define the entropy as

$$S = k \ln N(E, a), \tag{13.1}$$

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

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

or

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

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

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

the trace of which is

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

As before, we need to define smoothed quantities:

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

so, according to Eq. (11.17),

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

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

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

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

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

according to Eq. (11.30).

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

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

Now from Eq. (13.4)

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

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

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

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

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

or

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

or

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

or

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

which is the first law of thermodynamics, once again.

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

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

We further recall from Eq. (6.7)

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

or

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

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