

Chapter 8

Entropy II

We now turn to the definition of entropy in the microcanonical ensemble. Recall there

$$\rho(p, q) = \frac{\delta(E - H)}{\Omega(E)}. \quad (8.1)$$

Recall, further, we had defined the characteristic function

$$\psi_E(H) = \begin{cases} 1, & H < E \\ 0, & H > E \end{cases} = \int_H^\infty \delta(E - E') dE'. \quad (8.2)$$

Suppose the Hamiltonian depends on some parameter a , say, the size of a box containing a gas. Then

$$\frac{\partial}{\partial a} \psi_E(H) = -\delta(E - H) \frac{\partial H}{\partial a}, \quad (8.3)$$

and the “average force” is given by

$$\begin{aligned} \bar{\mathcal{F}}_a &= -\left\langle \frac{\partial H}{\partial a} \right\rangle = -\frac{1}{\Omega(E, a)} \int \delta(E - H(p, q, a)) \frac{\partial H}{\partial a} dp dq \\ &= \frac{1}{\Omega(E, a)} \frac{\partial}{\partial a} \int \psi_E(H(p, q, a)) dp dq = \frac{1}{\Omega(E, a)} \frac{\partial}{\partial a} V(E, a), \end{aligned} \quad (8.4)$$

where $V(E, a)$ is the volume of phase space for which $H < E$. Recall from Eq. (3.19) that

$$\Omega(E, a) = \frac{\partial}{\partial E} V(E, a), \quad (8.5)$$

so the average force is given by

$$\bar{\mathcal{F}}_a = \frac{\frac{\partial}{\partial a} V(E, a)}{\frac{\partial}{\partial E} V(E, a)}. \quad (8.6)$$

Regard E and a as independent. Then a general change in V is

$$dV = \frac{\partial V}{\partial E} dE + \frac{\partial V}{\partial a} da = \Omega dE + \Omega \bar{\mathcal{F}}_a da, \quad (8.7)$$

or

$$\frac{dV}{\Omega} = dE + \bar{\mathcal{F}}_a da. \quad (8.8)$$

This we interpret as the *First Law of Thermodynamics*, with the identifications

$$dE = dU, \quad \bar{\mathcal{F}}_a da = \delta W, \quad \delta Q = \frac{dV}{\Omega}, \quad (8.9)$$

so

$$\delta Q = dU + \delta W. \quad (8.10)$$

The *Second Law of Thermodynamics* says that although δQ is not an exact differential, it has an integrating factor, λ , which defines the entropy,

$$\lambda \delta Q = dS, \quad (8.11)$$

which is the same for all systems in equilibrium with each other, and $\lambda = 1/T$, where T is the absolute temperature.

Incidentally, note that if you've seen one integrating factor you've seen them all. That is, if

$$\frac{\delta Q}{T} = dS, \quad (8.12)$$

then $F'(S)/T$ is also an integrating factor, for any function F :

$$F'(S) \frac{\delta Q}{T} = dF(S). \quad (8.13)$$

The first law then reads

$$TdS = dU + \bar{\mathcal{F}}_a da, \quad (8.14)$$

or

$$\left(\frac{\partial S}{\partial U} \right)_a = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial a} \right)_U = \frac{1}{T} \bar{\mathcal{F}}_a. \quad (8.15)$$

What is the entropy S ? Let's assume $S = S(V)$. Then

$$\frac{1}{T} = S' \frac{\partial V}{\partial E} = S' \Omega, \quad (8.16)$$

and

$$\frac{\partial S}{\partial a} = S' \Omega \frac{1}{\Omega} \frac{\partial V}{\partial a} = S' \frac{\partial V}{\partial a}, \quad (8.17)$$

which is an identity. A natural choice, reminiscent of what we did in the canonical ensemble, is

$$S = k \ln V, \quad (8.18)$$

which is the relation claimed in Eq. (3.21). Remember in Problem 2.2 we showed that the volume of an n -sphere, for large n , is concentrated very near the surface. So

$$V \approx \frac{\partial V}{\partial E} \Delta E, \quad (8.19)$$

where

$$\frac{\Delta E}{E} \sim \frac{1}{n}, \quad (8.20)$$

where n is the number of degrees of freedom. But by equipartition,

$$\frac{E}{n} \sim kT = \frac{1}{\beta}, \quad (8.21)$$

so up to an irrelevant multiplicative factor,

$$V = \frac{\Omega(E, a)}{\beta} (1 + O(1/n)). \quad (8.22)$$

Therefore, the entropy may also be written in terms of

$$\ln V = \ln \Omega(E, a) - \ln \beta. \quad (8.23)$$

$\ln \beta$ is independent of n , while $\ln \Omega = O(n)$, so we can equally well use

$$S = k \ln \Omega(E, a). \quad (8.24)$$

This again is just the statement that the volume is concentrated very near the surface.

8.1 Ideal Gas

Recall Chapter 5, about the ideal gas. The structure function is

$$\begin{aligned} \Omega &= V^N \int \delta \left(E - \frac{1}{2m} \sum_{j=1}^{3N} p_j^2 \right) A_{3N} p^{3N-1} dp \\ &= V^N \frac{2m}{2\sqrt{2mE}} A_{3N} (2mE)^{(3N-1)/2} \\ &= mV^N (2mE)^{(3N-2)/2} 2 \frac{\pi^{3N/2}}{\Gamma(3N/2)}, \end{aligned} \quad (8.25)$$

where we used Eq. (5.16). The entropy is

$$S = k \ln \Omega = kN \ln \left[V(2\pi mE)^{3/2} \right] - \frac{3}{2} kN \left(\ln \frac{3N}{2} - 1 \right) + \dots, \quad (8.26)$$

where we used the Stirling approximation; the omitted terms are independent of N . Using $E = \frac{3}{2} NkT$, we see

$$S = kN \left[\ln V + \frac{3}{2} \ln(2\pi mkT) + \frac{3}{2} \right], \quad (8.27)$$

which is exactly the result found in Eqs (6.37) and (6.36),

$$S = \frac{1}{T} U + k \ln Z = \frac{3}{2} Nk + kN \left[\ln V + \frac{3}{2} \ln(2\pi mkT) \right]. \quad (8.28)$$