Chapter 3

Equipartition Theorem

The *Equipartition Theorem* is a fundamental result of classical statistical mechanics. We only need suppose $\rho = \rho(H)$. Then, define

$$\Theta(E) = \int_E^\infty dE' \rho(E'), \tag{3.1}$$

where in order that the integral exist, we require $\rho(E) \to 0$ as $E \to \infty$. Then

$$\frac{d\Theta}{dE} = -\rho(E). \tag{3.2}$$

Now consider

$$\begin{aligned} \langle p_1 \frac{\partial H}{\partial p_1} \rangle &= \int \rho(H) p_1 \frac{\partial H}{\partial p_1} dq\, dp \\ &= -\int p_1 \frac{d\Theta}{dE} \frac{\partial H}{\partial p_1} dq\, dp \\ &= -\int p_1 \frac{\partial \Theta}{\partial p_1} dq\, dp \\ &= \int \Theta(H)\, dq\, dp - \int \frac{\partial}{\partial p_1} \left(p_1 \Theta(H)\right) dq\, dp. \end{aligned} \tag{3.3}$$

The last integral, coming from integration by parts, vanishes because $\Theta \to 0$ as $|p_1| \to \infty$. Thus we conclude, for each degree of freedom

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = \int \Theta(H)\, dq\, dp, \tag{3.4}$$

the same for all p_i. By exactly the same argument, we have similarly

$$\langle q_i \frac{\partial H}{\partial q_i} \rangle = \int \Theta(H)\, dq\, dp. \tag{3.5}$$

This assumes that none of the coordinates are cyclic ones, like an angle φ, but, say, Cartesian coordinates.

For example, if we use the canonical distribution,

$$\rho = \frac{1}{Z} e^{-\beta H}, \tag{3.6}$$

the characteristic function is

$$\Theta(E) = \frac{1}{Z} \int_E^\infty e^{-\beta E'} dE' = \frac{1}{Z} \frac{1}{\beta} e^{-\beta E}, \tag{3.7}$$

and

$$\int \Theta(E)\, dq\, dp = \frac{1}{\beta} = kT. \tag{3.8}$$

(In general, as we'll see below, this same result must hold whatever distribution we choose.)

The equipartition theorem is usually stated for "quadratic degrees of freedom," that is, where the Hamiltonian has the form, for example,

$$H = \frac{1}{2} \frac{p_1^2}{m} + \frac{1}{2} k q_1^2 + \dots. \tag{3.9}$$

Then

$$p_1 \frac{\partial H}{\partial p_1} = \frac{p_1^2}{m} \equiv 2H(p_1), \quad q_1 \frac{\partial H}{\partial q_1} = k q_1^2 \equiv 2H(q_1), \tag{3.10}$$

so

$$\langle H(p_1) \rangle = \langle H(q_1) \rangle = \frac{1}{2} kT. \tag{3.11}$$

To illustrate the universality of this result, consider instead the microcanonical ensemble,

$$\rho(H) = \frac{1}{\Omega(E)} \delta(E - H). \tag{3.12}$$

Then the characteristic function is

$$\Theta(H) = \int_H^\infty \rho(E')\, dE' = \frac{1}{\Omega(E)} \int_H^\infty \delta(E' - E)\, dE' = \frac{1}{\Omega(E)} \psi_E(H), \tag{3.13}$$

where

$$\psi_E(H) = \begin{cases} 0, & H > E, \\ 1, & H < E. \end{cases} \tag{3.14}$$

Then the quantity which appears on the right-hand-side of the equipartition theorem (3.4) and (3.5) is

$$\int \Theta(H)\, dq\, dp = \frac{1}{\Omega(E)} V(E), \tag{3.15}$$

where $V(E)$ is the volume of phase space which has $H < E$,

$$V(E) = \int \psi_E(H(q, p))\, dq\, dp. \tag{3.16}$$

Now, because $\psi_E(H)$ is a step function,

$$\frac{d\psi_E(H)}{dE} = \delta(E - H), \tag{3.17}$$

as may be verified by integration:

$$\int_{H-\epsilon}^{H+\epsilon} \frac{d\psi_E(H)}{dE} dE = \psi_{H+\epsilon}(H) - \psi_{H-\epsilon}(H) = 1 = \int_{H-\epsilon}^{H+\epsilon} \delta(E - H)\, dE, \tag{3.18}$$

where ϵ is a vanishingly small positive number. Then we conclude

$$\begin{aligned} \Omega(E) &= \int \delta(E - H)\, dq\, dp = \int \frac{d}{dE}\psi_E(H)\, dq\, dp \\ &= \frac{d}{dE}\int \psi_E(H)\, dq\, dp = \frac{d}{dE}V(E). \end{aligned} \tag{3.19}$$

Therefore, the equipartition theorem (3.4) reads

$$\begin{aligned} \langle p_i \frac{\partial H}{\partial p_i} \rangle &= \int \Theta(H)\, dq\, dp = \frac{V(E)}{\frac{d}{dE}V(E)} \\ &= \frac{1}{\frac{d}{dE}\ln V(E)}. \end{aligned} \tag{3.20}$$

Now, we will see that

$$\ln V(E) = \frac{1}{k} S, \tag{3.21}$$

where S is the entropy and k is Boltzmann's constant, a unit conversion factor. Further, we have the thermodynamic relation $dS/dE = 1/T$, so the equipartition theorem reads

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = kT. \tag{3.22}$$

[Properly, we should measure T not in Kelvins, but in ergs or electron-volts, so that $k = 1$.]