

7.D.1. Probability Density Operator

The set of systems, each representing one of the allowed independent microstates of a thermodynamic system, is called an **ensemble**. Thus, average over the ensemble is equivalent to the average over all possible microstates that conform to the constraints on the actual system.

Alternatively, one may imagine placing all member systems of the ensemble together to form one big system. If the member systems interact with each other the same way that the actual system acts with its environment, then the rest of the member systems will serve as the environment of a given member system. Equilibrium of the combined system is then equivalent to the equilibrium of the actual system with its environment.

For a system of infinite extent, members of the ensemble can be taken as subsystems of the system itself.

For a closed system that can exchange heat with its environment, the corresponding ensemble is called a **canonical ensemble**. Since heat exchange is allowed, the environment serves as a heat reservoir of a fixed temperature T , which serves as the defining characteristic of the ensemble.

From the microscopic point of view, heat exchange is just energy exchange. Equilibrium is therefore established when the average energy is a constant, i.e.,

$$\langle H \rangle \equiv \text{Tr}_N(\hat{H}_N \hat{\rho}) = U = \text{const.} \quad (7.38)$$

Macroscopically, equilibrium means the entire system is at the same uniform temperature T .

According to the 2nd law, entropy is maximized at equilibrium. Thus, the equilibrium probability density operator is the solution to

$$\delta S = -k_B \delta \text{Tr}(\hat{\rho} \ln \hat{\rho}) = 0 \quad (7.37a)$$

under the constraints

$$\text{Tr}_N \hat{\rho} = 1 \quad \& \quad \text{Tr}_N(\hat{H}_N \hat{\rho}) = U \quad (7.37)$$

Removing the constraints via the Lagrange multipliers α_0 & α_E , we have

$$\begin{aligned} & \delta \text{Tr}_N \left[-k_B \hat{\rho} \ln \hat{\rho} + \alpha_0 \hat{\rho} + \alpha_E \hat{H}_N \hat{\rho} \right] = 0 \\ \rightarrow & \text{Tr}_N \left[-k_B (\ln \hat{\rho} + \hat{1}) \delta \hat{\rho} + \alpha_0 \delta \hat{\rho} + \alpha_E \hat{H}_N \delta \hat{\rho} \right] = 0 \end{aligned} \quad (7.39)$$

where $\hat{1}$ is the identity (or unit) operator.

Since $\delta \hat{\rho}$ is arbitrary, (7.39) can be satisfied only if

$$-k_B (\ln \hat{\rho} + \hat{1}) + \alpha_0 \hat{1} + \alpha_E \hat{H}_N = 0 \quad (7.40)$$

$$\rightarrow \hat{\rho} = \exp \left(-1 + \frac{1}{k_B} \alpha_0 \right) \exp \left(\frac{\alpha_E}{k_B} \hat{H}_N \right) \quad (7.41)$$

The prefactor can be taken as a normalization constant and determined by the normalization condition

$$\text{Tr}_N \hat{\rho} = \exp \left(-1 + \frac{1}{k_B} \alpha_0 \right) \text{Tr}_N \exp \left(\frac{\alpha_E}{k_B} \hat{H}_N \right) = 1$$

It is customary to define the **partition function** as

$$Z_N \equiv \text{Tr}_N \exp \left(\frac{\alpha_E}{k_B} \hat{H}_N \right) = \exp \left(1 - \frac{1}{k_B} \alpha_0 \right) \quad (7.42)$$

so that (7.41) becomes

$$\hat{\rho} = \frac{1}{Z_N} \exp\left(\frac{\alpha_E}{k_B} \hat{H}_N\right) \quad (7.42a)$$

The multiplier α_E can be determined using thermodynamic relations. Thus, $\text{Tr}_N[\hat{\rho}(7.40)]$ gives

$$\text{Tr}_N[-k_B \hat{\rho} \ln \hat{\rho} + \hat{\rho}(-k_B + \alpha_0) + \alpha_E \hat{\rho} \hat{H}_N] = 0$$

$$\rightarrow S - k_B + \alpha_0 + \alpha_E U = 0$$

$$S - k_B \ln Z_N + \alpha_E U = 0 \quad [(7.42) \text{ used.}] \quad (7.43)$$

Comparing (7.43) with the only 3-term thermodynamic relation that involves U & S , namely,

$$A = U - TS$$

we have

$$\alpha_E = -\frac{1}{T}$$

and

$$A = -k_B T \ln Z_N \quad (7.44)$$

(7.42-a) thus become

$$Z_N = \text{Tr}_N \exp\left(-\frac{1}{k_B T} \hat{H}_N\right) = \text{Tr}_N \exp(-\beta \hat{H}_N) \quad \left[\beta = \frac{1}{k_B T}\right] \quad (7.45)$$

$$= e^{-\beta A} \quad [(7.44) \text{ used.}] \quad (7.45a)$$

and

$$\hat{\rho} = \frac{1}{Z_N} \exp(-\beta \hat{H}_N) \quad (7.46)$$

$$= \exp[-\beta(\hat{H}_N - A)] \quad (7.46a)$$

(7.44) is the link between statistical mechanics and thermodynamics. Once Z_N is obtained, so is A , and hence all the other thermodynamic quantities.

Since the average energy is fixed at $\langle H \rangle = U$, it is of interest to find the magnitude of the fluctuations about this value. In other words, we wish to calculate the variance

$$\text{var}(H) = \langle H^2 \rangle - \langle H \rangle^2$$

Consider now the partition function (7.45).

$$\frac{\partial Z_N}{\partial \beta} = -\text{Tr}_N[\hat{H}_N \exp(-\beta \hat{H}_N)] = -Z_N \langle H \rangle$$

$$\frac{\partial^2 Z_N}{\partial \beta^2} = \text{Tr}_N[\hat{H}_N^2 \exp(-\beta \hat{H}_N)] = Z_N \langle H^2 \rangle$$

and in general,

$$\langle H^n \rangle = (-)^n \frac{1}{Z_N} \frac{\partial^n Z_N}{\partial \beta^n} \quad (7.49a)$$

$$\begin{aligned} \rightarrow \text{var}(H) &= \frac{1}{Z_N} \frac{\partial^2 Z_N}{\partial \beta^2} - \left(\frac{1}{Z_N} \frac{\partial Z_N}{\partial \beta}\right)^2 \\ &= e^{\beta A} \frac{\partial^2 e^{-\beta A}}{\partial \beta^2} - \left(e^{\beta A} \frac{\partial e^{-\beta A}}{\partial \beta}\right)^2 \quad [(7.45a) \text{ used.}] \\ &= e^{\beta A} \frac{\partial}{\partial \beta} \left[-\frac{\partial(\beta A)}{\partial \beta} e^{-\beta A}\right] - \left[-\frac{\partial(\beta A)}{\partial \beta}\right]^2 \\ &= -\frac{\partial^2(\beta A)}{\partial \beta^2} \\ &= -\frac{\partial}{\partial \beta} \left(A + \beta \frac{\partial A}{\partial \beta}\right) \end{aligned}$$

$$\begin{aligned}
&= -2 \frac{\partial A}{\partial \beta} - \beta \frac{\partial^2 A}{\partial \beta^2} \\
&= -2 \frac{\partial T}{\partial \beta} \frac{\partial A}{\partial T} - \beta \frac{\partial T}{\partial \beta} \frac{\partial}{\partial T} \left(\frac{\partial T}{\partial \beta} \frac{\partial A}{\partial T} \right) \quad \left[\frac{\partial T}{\partial \beta} = -k_B T^2 \text{ used.} \right] \\
&= 2 k_B T^2 \frac{\partial A}{\partial T} - k_B T \frac{\partial}{\partial T} \left(T^2 \frac{\partial A}{\partial T} \right) \\
&= -k_B T^3 \frac{\partial^2 A}{\partial T^2} \tag{7.49b}
\end{aligned}$$

For a closed system, $N = \text{const.}$ If we also assume $V = \text{const.}$, then (7.49b) becomes, for a PVT system,

$$\begin{aligned}
\text{var}(H) &= -k_B T^3 \left(\frac{\partial^2 A}{\partial T^2} \right)_{NV} \\
&= k_B T^3 \left(\frac{\partial S}{\partial T} \right)_{NV} \\
&= k_B T^2 C_V \tag{7.49}
\end{aligned}$$

where C_V is the heat capacity at constant volume. Since

$$U, S \propto N \quad \rightarrow \quad C_V \propto N$$

we have

$$\frac{\sigma_H}{U} = \frac{\sqrt{\text{var}(H)}}{U} \propto \frac{\sqrt{N}}{N} \propto \frac{1}{\sqrt{N}} \xrightarrow{N \rightarrow \infty} 0 \tag{7.50}$$

Thus, the fluctuations in energy is negligible in the thermodynamic limit. This means the canonical ensemble is effectively the same as the microcanonical ensemble as $N \rightarrow \infty$.