

## 7.B. The Microcanonical Ensemble

A system is

**closed** if there is no particle exchange with its environment,

and

**isolated** if there is no energy exchange with its environment,

Hence, both  $N$  (total number of particles) and  $E$  (total energy) are conserved for a closed and isolated system. Possible states of the system therefore lie on the hypersurface  $\Sigma_E$  of constant  $E$  in the  $N$ -particle phase space.

For an ergodic system, time average is the same as phase space average. Therefore, if an ergodic system is also closed and isolated, the probability of finding the system in any one of the states on  $\Sigma_E$  must be the same.

For a quantum system, since the equilibrium state is necessarily stationary (time-independent), the Liouville equation (6.53) requires the probability density operator to be a function of the Hamiltonian only, i.e.,  $\hat{\rho} = \hat{\rho}(\hat{H})$  [ see (6.59) ]. Let  $\mathcal{N}(E)$  be the total number of states with energy  $E$ . The corresponding eigenstates of  $\hat{H}$  is denoted by the orthonormal set

$$\{ | E, n \rangle ; n = 1, \dots, \mathcal{N}(E) \} \quad \langle E, n | E, m \rangle = \delta_{nm} \quad (7.3a)$$

The **Gibbs entropy** is defined as

$$S = -k_B \text{Tr}(\hat{\rho} \ln \hat{\rho}) \quad (7.3)$$

where

$$k_B \approx 1.38 \times 10^{-23} \text{ J / K} \approx 8.62 \times 10^{-5} \text{ eV / K}$$

is the **Boltzmann constant**.

For a closed and isolated system of total energy  $E$ , (7.3) simplifies to

$$\begin{aligned} S &= -k_B \sum_{n=1}^{\mathcal{N}(E)} \langle E, n | \hat{\rho} \ln \hat{\rho} | E, n \rangle \\ &= -k_B \sum_{n,m=1}^{\mathcal{N}(E)} \langle E, n | \hat{\rho} | E, m \rangle \langle E, m | \ln \hat{\rho} | E, n \rangle \\ &= -k_B \sum_{n,m=1}^{\mathcal{N}(E)} \delta_{nm} P_n \ln P_n \\ &= -k_B \sum_{n=1}^{\mathcal{N}(E)} P_n \ln P_n \end{aligned} \quad (7.4)$$

where

$$P_n = \langle E, n | \hat{\rho} | E, n \rangle = \text{probability of finding the system in state } | E, n \rangle.$$

According to the 2nd law of thermodynamics, the equilibrium state is at a maximum of  $S$ . Hence, the equilibrium value of  $P_n$  can be determined by the extremum condition

$$\delta S = 0 \quad (7.4a)$$

under the normalization constraint

$$\text{Tr} \hat{\rho} = \sum_{n=1}^{\mathcal{N}(E)} P_n = 1 \quad (7.4b)$$

Transforming the variation to an unconstrained one via the Lagrange multiplier  $\alpha_0$  gives

$$\delta \left[ -k_B \sum_{n=1}^{\mathcal{N}(E)} P_n \ln P_n + \alpha_0 \left( \sum_{n=1}^{\mathcal{N}(E)} P_n - 1 \right) \right] = 0$$

$$\rightarrow \sum_{n=1}^{\mathcal{N}(E)} \delta \left( -k_B P_n \ln P_n + \alpha_0 P_n \right) = 0$$

$$\sum_{n=1}^{\mathcal{N}(E)} \left( -k_B \ln P_n - k_B + \alpha_0 \right) \delta P_n = 0 \quad \left[ \delta \ln P_n = \frac{1}{P_n} \delta P_n \text{ used.} \right] \quad (7.5)$$

Since the  $\delta P_n$ 's are independent of each other, we have

$$-k_B \ln P_n - k_B + \alpha_0 = 0 \quad \forall n$$

$$\rightarrow P_n = \exp \left( -1 + \frac{\alpha_0}{k_B} \right) \quad (7.6)$$

is the same for all  $n$ . The normalization (7.4b) then gives

$$P_n = \frac{1}{\mathcal{N}(E)} \quad (7.7)$$

which agrees with the result for an ergodic system.

The probability distribution given by (7.7) is called the **microcanonical ensemble**.

Putting (7.7) into (7.4) gives

$$S = k_B \sum_{n=1}^{\mathcal{N}(E)} \frac{1}{\mathcal{N}(E)} \ln \mathcal{N}(E)$$

$$= k_B \ln \mathcal{N}(E) \quad (7.8)$$

### Ex. 7.1.

An **Einstein solid** is a  $d$ -D lattice with an independent  $d$ -D harmonic oscillator of frequency  $\omega$  at each site.

Since there are no interactions between the oscillators,

$$H = \hbar \omega \sum_{i=1}^{dN} \left( n_i + \frac{1}{2} \right) = E \quad (1a)$$

where  $N$  is the total number of sites and  $n_i$  is the excitation ( number of quanta ) at site  $i$ . Note that  $H$  depends only on the total number of quanta

$$M = \sum_{i=1}^{dN} n_i \quad (1b)$$

since

$$H = \hbar \omega \left( M + \frac{1}{2} dN \right) = E \quad (1c)$$

The microcanonical ensemble then assumes  $E$ , & hence,  $M$  constant.

Thus, if we treat the quanta as particles, then the number of particles is also fixed. However, this is simply a coincidence due to the special relation (1c). The number of vibrational quanta ( vibrons or phonons ) are in general not conserved.

On the other hand, in classical mechanics, as well as the treatment described below, the oscillators themselves are taken as the "particles".

Assume  $M$  &  $N$  are large.

(a) What is the total number of microscopic states with energy  $E$ ?

- (b) Compute  $S$  as a function of  $T$  and  $N$ .  
 (c) Compute the heat capacity of this solid.

### Answer (a)

By (1c),  $\mathcal{N}(E)$  is equal to the number of ways to assign  $M$  indistinguishable quanta to  $dN$  distinguishable oscillators, i.e., the number of ways of putting  $M$  identical balls into a line of  $dN$  boxes. The latter is in turn equivalent to the distinctive permutations of  $M + dN - 1$  objects, composed of  $M$  balls and  $dN - 1$  interior partitions, and arranged on a line. Thus

$$\mathcal{N}(E) = \frac{(M + dN - 1)!}{M!(dN - 1)!} \quad (1)$$

### Answer (b)

Putting (1) into (7.8), we have

$$S = k_B \ln \frac{(M + dN - 1)!}{M!(dN - 1)!} \quad (2)$$

For  $M$  &  $N$  large, the **Stirling formula**

$$\ln N! \approx N \ln N - N \quad \text{for} \quad N \gg 1 \quad (2a)$$

turns (2) into

$$\begin{aligned} S &\approx k_B [(M + dN - 1) \ln (M + dN - 1) - (M + dN - 1) \\ &\quad - M \ln M + M - (dN - 1) \ln (dN - 1) + (dN - 1)] \\ &= k_B [(M + dN - 1) \ln (M + dN - 1) - M \ln M - (dN - 1) \ln (dN - 1)] \\ &\approx k_B [(M + dN) \ln (M + dN) - M \ln M - (dN) \ln (dN)] \quad [1\text{'s dropped.}] \\ &= k_B \ln \left[ \frac{(M + dN)^{M + dN}}{M^M (dN)^{dN}} \right] \\ &= k_B \ln \left( \frac{\left( \frac{M}{dN} + 1 \right)^{M + dN}}{\left( \frac{M}{dN} \right)^M} \right) \end{aligned} \quad (3)$$

Treating the oscillators as particles, we have [ see (2.68) of §2.F.1 ]

$$\begin{aligned} T &= \left( \frac{\partial E}{\partial S} \right)_N \\ &= \hbar \omega \left( \frac{\partial M}{\partial S} \right)_N \quad [(1c) \text{ used.}] \\ &= \frac{\hbar \omega}{\left( \frac{\partial S}{\partial M} \right)_N} \end{aligned} \quad (4a)$$

(3) gives [ see *Mathematica* code below ]

$$\begin{aligned} \left( \frac{\partial S}{\partial M} \right)_N &= k_B \ln \left( \frac{M + dN}{M} \right) \\ &= k_B \ln \left( 1 + \frac{dN}{M} \right) \end{aligned} \quad (4)$$

$$= \frac{\hbar \omega}{T} \quad [(4a) \text{ used.}]$$

$$\ln[*]= s = k \text{Log} \left[ \frac{\binom{M+n}{n}^{M+n}}{\binom{M}{n}^M} \right];$$

$\partial_M s$  // Simplify

$$\text{Out[*]}= k \left( -\text{Log} \left[ \frac{M}{n} \right] + \text{Log} \left[ \frac{M+n}{n} \right] \right)$$

Solving (4) for  $M$  gives

$$1 + \frac{dN}{M} = e^{\beta \hbar \omega} \quad \beta = \frac{1}{k_B T}$$

$$\rightarrow M = \frac{dN}{e^{\beta \hbar \omega} - 1} \quad (5)$$

$$\therefore 1 + \frac{M}{dN} = 1 + \frac{1}{e^{\beta \hbar \omega} - 1} = \frac{e^{\beta \hbar \omega}}{e^{\beta \hbar \omega} - 1} = \frac{1}{1 - e^{-\beta \hbar \omega}}$$

$$M + dN = \left( \frac{1}{e^{\beta \hbar \omega} - 1} + 1 \right) dN = \frac{e^{\beta \hbar \omega}}{e^{\beta \hbar \omega} - 1} dN \quad (5a)$$

$$= k_B \ln \left( \frac{\left( \frac{M}{dN} + 1 \right)^{M+dN}}{\left( \frac{M}{dN} \right)^M} \right)$$

Putting these back into (3) gives

$$\begin{aligned} S &= k_B \ln \left( \frac{\left( \frac{1}{1 - e^{-\beta \hbar \omega}} \right)^{M+dN}}{\left( \frac{1}{e^{\beta \hbar \omega} - 1} \right)^M} \right) \\ &= dN k_B \ln(1 - e^{-\beta \hbar \omega}) + M k_B \ln \frac{e^{\beta \hbar \omega} - 1}{1 - e^{-\beta \hbar \omega}} \\ &= dN k_B \ln(1 - e^{-\beta \hbar \omega}) + M k_B \beta \hbar \omega \\ &= dN k_B \ln(1 - e^{-\beta \hbar \omega}) + dN k_B \frac{\beta \hbar \omega}{e^{\beta \hbar \omega} - 1} \quad [(5) \text{ used.}] \\ &= dN k_B \ln(1 - e^{-\beta \hbar \omega}) + dN k_B \frac{\beta \hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \\ &= dN k_B \left[ \ln(1 - e^{-\beta \hbar \omega}) + \frac{\beta \hbar \omega}{e^{\beta \hbar \omega} - 1} \right] \end{aligned} \quad (6)$$

Similarly, putting (5) into (1c) gives

$$\begin{aligned} U = E &= \hbar \omega \left( \frac{dN}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} dN \right) \\ &= \frac{dN \hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} + \frac{1}{2} dN \hbar \omega \\ &= dN \hbar \omega \left( \frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right) \end{aligned} \quad (7)$$

Answer (c)

The heat capacity is

$$\begin{aligned}
 C_N &= \left( \frac{dQ}{dT} \right)_N = T \left( \frac{\partial S}{\partial T} \right)_N \\
 &= dN k_B T \left[ \frac{\hbar \omega}{k_B T^2} \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} - \frac{1}{k_B T^2} \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} + \frac{\hbar \omega}{k_B T^2} \frac{\beta \hbar \omega e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \right] \\
 &\hspace{15em} \text{[ (6) used. ]} \\
 &= dN k_B T \frac{\hbar \omega}{k_B T^2} \frac{\beta \hbar \omega e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \\
 &= dN \frac{(\hbar \omega)^2}{k_B T^2} \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} \\
 &= dN \frac{(\hbar \omega)^2}{k_B T^2} \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2} \tag{8}
 \end{aligned}$$

----- Ex. 7.1. ends -----

The classical version of the foregoing discussion is as follows.

To begin, the Gibbs entropy [ c.f. (7.3) ] is defined as

$$S = -k_B \int d\Gamma_N \rho(\mathbf{X}^N) \ln[ C_N \rho(\mathbf{X}^N) ] \tag{7.2}$$

where

$\mathbf{X}^N = (\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$  = phase space coordinates of an  $N$  particle system

$d\Gamma_N = d^{2dN} \mathcal{X} = d^d q_1 \dots d^d q_N d^d p_1 \dots d^d p_N$

= phase space volume element of a  $d$ -D system

At first,  $C_N$  is merely a constant required to keep the argument of the logarithm,  $C_N \rho(\mathbf{X}^N)$ , dimensionless. Nowadays, it is called the **Gibbs counting factor**, after Gibbs used it to resolve the Gibbs paradox [ see §S2.B ]. Its value can be obtained by comparing the ideal gas results with the (exact) quantum mechanical results. Thus [ see §7.D ],

$$\frac{C_N}{h^{3N}} = \begin{cases} 1 & \text{for distinguishable particles} \\ N! & \text{for indistinguishable particles} \end{cases} \tag{7.9a}$$

where

$$h \approx 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \approx 4.14 \times 10^{-15} \text{ eV} \cdot \text{s}$$

is the **Planck's constant**.

For a closed and isolated system, all possible states must lie on the constant energy hypersurface  $\Sigma_N(E)$ . The requirement that  $S$  must be a maximum for a system in equilibrium thus becomes

$$\delta S = 0$$

subject to the normalization constraint

$$\int d\Gamma_N \rho(\mathbf{X}^N) = \int d\Sigma_N(E) \sigma_E(\mathbf{X}^N) = 1 \tag{7.9}$$

where  $\sigma_E(\mathbf{X}^N)$  is the surface probability density on the hypersurface  $\Sigma_N(E)$ .

Using

$$\lim_{x \rightarrow 0} x \ln x = 0$$

(7.2) becomes

$$S = -k_B \int d\Sigma_N(E) \sigma_E(\mathbf{X}^N) \ln \left[ \frac{C_N}{\Delta \mathcal{X}_E} \sigma_E(\mathbf{X}^N) \right] \tag{7.2a}$$

where the constant  $\Delta X_E$  of dimension  $|\mathbf{X}^N|$  is inserted to keep the argument of the logarithm dimensionless. Later on, we shall interpret it as the average distance between the hypersurfaces  $H = E$  &  $H = E - \Delta E$ , where  $H = H(\mathbf{X}^N)$  is the Hamiltonian.

With the help of the Lagrange multiplier  $\alpha_0$ , we have

$$\int d\Sigma_N(E) \delta \left\{ -k_B \sigma_E(\mathbf{X}^N) \ln \left[ \frac{C_N}{\Delta X_E} \sigma_E(\mathbf{X}^N) \right] + \alpha_0 \sigma_E(\mathbf{X}^N) \right\} = 0 \quad (7.10)$$

$$\rightarrow -k_B \delta \sigma_E(\mathbf{X}^N) \ln \left[ \frac{C_N}{\Delta X_E} \sigma_E(\mathbf{X}^N) \right] - k_B \delta \sigma_E(\mathbf{X}^N) + \alpha_0 \delta \sigma_E(\mathbf{X}^N) = 0$$

$$\therefore -k_B \ln \left[ \frac{C_N}{\Delta X_E} \sigma_E(\mathbf{X}^N) \right] - k_B + \alpha_0 = 0$$

$$\sigma_E(\mathbf{X}^N) = \frac{\Delta X_E}{C_N} \exp \left( -1 + \frac{\alpha_0}{k_B} \right) \equiv C_E \quad \forall \mathbf{X}^N \in \Sigma_N(E) \quad (7.11a)$$

The constant  $C_E$  is determined by (7.9) as

$$\int d\Sigma_N(E) C_E = 1 \quad \rightarrow \quad C_E = \frac{1}{\Sigma_N(E)} \quad (7.11b)$$

(7.2a) becomes

$$\begin{aligned} S &= -k_B \int d\Sigma_N(E) \frac{1}{\Sigma_N(E)} \ln \left[ \frac{C_N}{\Delta X_E \Sigma_N(E)} \right] \\ &= \ln \left[ \frac{\Delta X_E \Sigma_N(E)}{C_N} \right] \end{aligned} \quad (7.12)$$

In practice, it is easier to work with

$$\Omega_N(E) = \int_{U=0}^{U=E} dX_E \Sigma_N(U) = \int_0^E dU \frac{1}{\left| \nabla_{\mathbf{X}^N} H \right|_{H=U}} \Sigma_N(U) \quad (7.13)$$

= volume of phase space for states with internal energy  $U \leq E$ .

The last expression in (7.13) is obtained using the definition of the gradient vector,

$$dH = \nabla_{\mathbf{X}^N} H \cdot d\mathbf{X}^N = \left| \nabla_{\mathbf{X}^N} H \right|_{H=E} dX_E$$

where  $d\mathbf{X}^N$  is an infinitesimal displacement in the phase space and  $dX_E = \hat{\mathbf{n}}_H \cdot d\mathbf{X}^N$  its component along the normal  $\hat{\mathbf{n}}_H$  of the hypersurface  $H = E$ .

Since  $\Sigma_N(E)$  is the area of a hypersurface, it must be a non-negative quantity. Therefore,

$$\Sigma_N(E) = \left| \nabla_{\mathbf{X}^N} H \right|_{H=E} \frac{d\Omega_N(E)}{dE} \geq 0 \quad (7.13a)$$

which means  $\Omega_N(E)$  is a monotonically increasing function of  $E$ . Hence,

$$\Omega_N(E) \geq \int_{U=E-\Delta E}^{U=E} dX_E \Sigma_N(U) \approx \Delta X_E \Sigma_N(E) \quad \Delta E \rightarrow 0 \quad (7.14a)$$

where  $\Delta X_E$  is the average distance between the hypersurfaces  $E$  &  $E - \Delta E$ . Furthermore, as  $E$  increases, the number of ways to share the energy between the particles increases. This means  $\Sigma_N(E)$  itself is also a monotonically increasing function of  $E$ . Thus, replacing  $\Sigma_N(U)$  with  $\Sigma_N(E)$  in (7.13) gives

$$\Omega_N(E) \leq \int_{U=0}^{U=E} dX_E \Sigma_N(E) = X_E \Sigma_N(E) \quad (7.14b)$$

where  $X_E$  is the distance between the hypersurfaces  $U = 0$  &  $U = E$ .

Combining (7.14a & b) gives

$$0 < \Delta X_E \Sigma_N(E) \leq \Omega_N(E) \leq X_E \Sigma_N(E)$$

$$\rightarrow \ln \left[ \Delta X_E \Sigma_N(E) \right] \leq \ln \Omega_N(E) \leq \ln \left[ \Delta X_E \Sigma_N(E) \right] + \ln \frac{X_E}{\Delta X_E} \quad (7.14c)$$

Since

$$\ln \Omega_N(E) \propto N \qquad \ln \frac{X_E}{\Delta X_E} \propto \ln N$$

(7.14c) becomes

$$n \left[ \Delta X_E \Sigma_N(E) \right] = \ln \Omega_N(E) \qquad \text{for } N \rightarrow \infty$$

so that (7.12) becomes

$$S = \ln \left[ \frac{\Omega_N(E)}{C_N} \right] \quad (7.16)$$

### Ex. 7.2.

Use the microcanonical ensemble to find the entropy and equation of state for an ideal gas of  $N$  identical particles of mass  $m$  in a box of volume  $V$ . Assume  $N$  &  $V$  to be very large.

### Answer

From Ex.6.2, we have

$$\Omega_N(E) = V^N \frac{(2\pi m E)^{3N/2}}{\Gamma\left(\frac{3}{2}N + 1\right)} \quad (1)$$

For very large  $N$  &  $V$ , (7.16) applies and we have

$$\begin{aligned} S &= k_B \ln \left( \frac{V^N (2\pi m E)^{3N/2}}{C_N \Gamma\left(\frac{3}{2}N + 1\right)} \right) \\ &= k_B \ln \left( \frac{V^N (2\pi m E)^{3N/2}}{N! h^{3N} \Gamma\left(\frac{3}{2}N + 1\right)} \right) \quad [(7.9a) \text{ used.}] \quad (2) \end{aligned}$$

Using the Stirling formula for large  $N$ ,

$$\ln N! \approx N \ln N - N \quad (2a)$$

we have

$$\begin{aligned} \Gamma\left(\frac{3}{2}N + 1\right) &= \left(\frac{3}{2}N\right)! = \exp\left[\ln\left(\frac{3}{2}N\right)!\right] \\ &\approx \exp\left[\frac{3}{2}N \ln\left(\frac{3}{2}N\right) - \frac{3}{2}N\right] \\ &= \left(\frac{3}{2}N\right)^{3N/2} e^{-3N/2} \\ &= \left(\frac{3}{2e}N\right)^{3N/2} \quad (2b) \end{aligned}$$

Putting (2b) into (2) gives

$$\frac{S}{k_B} \approx \ln \left[ \frac{V^N}{N! h^{3N}} \left( \frac{4}{3N} e \pi m E \right)^{3N/2} \right]$$

$$\begin{aligned}
&= N \ln\left(\frac{V}{h^3}\right) - \ln N! + \frac{3}{2} N \ln\left(\frac{4}{3N} e \pi m E\right) \\
&= N \ln\left[\frac{V}{h^3} \left(\frac{4}{3N} \pi m E\right)^{3/2}\right] - (N \ln N - N) + \frac{3}{2} N \quad [(2a) \text{ used.}] \\
&= \frac{5}{2} N + N \ln\left[\frac{V}{N} \left(\frac{4}{3h^2 N} \pi m E\right)^{3/2}\right] \quad (3)
\end{aligned}$$

or, in per-particle form,

$$\frac{s}{k_B} = \frac{5}{2} + \ln\left[v \left(\frac{4}{3h^2} \pi m \epsilon\right)^{3/2}\right] \quad (3a)$$

where

$$v = \frac{V}{N} \quad \& \quad \epsilon = \frac{E}{N}$$

Note that without the Gibbs counting factor,  $S$  cannot be written in the per-particle form.

The pressure is given by

$$\begin{aligned}
P &= -\left(\frac{\partial U}{\partial V}\right)_{S,N} \\
\left(\frac{\partial (3)}{\partial V}\right)_{S,N} &\text{ gives} \\
0 &= N \frac{\partial}{\partial V} \ln[V(U)^{3/2}] \\
&= N \left[ \frac{1}{V} + \frac{3}{2U} \left(\frac{\partial U}{\partial V}\right)_{S,N} \right] \\
\rightarrow PV &= \frac{2}{3} U \quad (3b)
\end{aligned}$$

The temperature is given by

$$\begin{aligned}
T &= \left(\frac{\partial U}{\partial S}\right)_{V,N} \\
\left(\frac{\partial (3)}{\partial S}\right)_{V,N} &\text{ gives} \\
\frac{1}{k_B} &= N \frac{\partial}{\partial S} \ln U^{3/2} \\
&= N \frac{3}{2U} \left(\frac{\partial U}{\partial S}\right)_{V,N} \\
\rightarrow U &= \frac{3}{2} N k_B T \quad (3c)
\end{aligned}$$

Combining (3b & c) gives

$$PV = N k_B T$$

which is the ideal gas equation (of state).