

4.4: Ordinary Canonical Ensemble (OCE)

Canonical Distribution and Partition Function

Consider a system S in contact with a world W , and let their union $U = W \cup S$ be called the ‘universe’. The situation is depicted in [Figure 4.4.1](#). The volume V_S and particle number N_S of the system are held fixed, but the energy is allowed to fluctuate by exchange with the world W . We are interested in the limit $N_S \rightarrow \infty$, $N_W \rightarrow \infty$, with $N_S \ll N_W$, with similar relations holding for the respective volumes and energies. We now ask what is the probability that S is in a state $|n\rangle$ with energy E_n . This is given by the ratio

$$P_n = \lim_{\Delta E \rightarrow 0} \frac{D_W(E_U - E_n) \Delta E}{D_U(E_U) \Delta E} \quad (4.4.1)$$

$$= \frac{\# \text{ of states accessible to } W \text{ given that } E_S = E_n}{\text{total } \# \text{ of states in } U} . \quad (4.4.2)$$

Then

$$\ln P_n = \ln D_W(E_U - E_n) - \ln D_U(E_U) \quad (4.4.3)$$

$$= \ln D_W(E_U) - \ln D_U(E_U) - E_n \left. \frac{\partial \ln D_W(E)}{\partial E} \right|_{E=E_U} + \dots \quad (4.4.4)$$

$$\equiv -\alpha - \beta E_n . \quad (4.4.5)$$

The constant β is given by

$$\beta = \left. \frac{\partial \ln D_W(E)}{\partial E} \right|_{E=E_U} = \frac{1}{k_B T} . \quad (4.4.6)$$

Thus, we find $P_n = e^{-\alpha} e^{-\beta E_n}$. The constant α is fixed by the requirement that $\sum_n P_n = 1$:

$$P_n = \frac{1}{Z} e^{-\beta E_n} , \quad Z(T, V, N) = \sum_n e^{-\beta E_n} = \text{Tr } e^{-\beta \hat{H}} . \quad (4.4.7)$$

We’ve already met $Z(\beta)$ in [Equation 3.3.4](#) – it is the Laplace transform of the density of states. It is also called the *partition function* of the system S . Quantum mechanically, we can write the ordinary canonical density matrix as

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\text{Tr } e^{-\beta \hat{H}}} , \quad (4.4.8)$$

which is known as the *Gibbs distribution*. Note that $[\hat{\rho}, \hat{H}] = 0$, hence the ordinary canonical distribution is a stationary solution to the evolution equation for the density matrix. Note that the OCE is specified by three parameters: T , V , and N .

The difference between $P(E_n)$ and P_n

Let the total energy of the Universe be fixed at E_U . The joint probability density $P(E_S, E_W)$ for the system to have energy E_S and the world to have energy E_W is

$$P(E_S, E_W) = D_S(E_S) D_W(E_W) \delta(E_U - E_S - E_W) / D_U(E_U) , \quad (4.4.9)$$

where

$$D_U(E_U) = \int_{-\infty}^{\infty} dE_S D_S(E_S) D_W(E_U - E_S) , \quad (4.4.10)$$

which ensures that $\int dE_S \int dE_W P(E_S, E_W) = 1$. The *probability density* $P(E_S)$ is defined such that $P(E_S) dE_S$ is the (differential) probability for the system to have an energy in the range $[E_S, E_S + dE_S]$. The units of $P(E_S)$ are E^{-1} . To obtain $P(E_S)$, we simply integrate the joint probability density $P(E_S, E_W)$ over all possible values of E_W , obtaining

$$P(E_S) = \frac{D_S(E_S) D_W(E_U - E_S)}{D_U(E_U)} , \quad (4.4.11)$$

as we have in Equation 4.4.1.

Now suppose we wish to know the probability P_n that the system is in a *particular* state $|n\rangle$ with energy E_n . Clearly

$$P_n = \lim_{\Delta E \rightarrow 0} \frac{\text{probability that } E_S \in [E_n, E_n + \Delta E]}{\text{\# of S states with } E_S \in [E_n, E_n + \Delta E]} = \frac{P(E_n) \Delta E}{D_S(E_n) \Delta E} = \frac{D_W(E_U - E_n)}{D_U(E_U)} . \quad (4.4.12)$$

Additional remarks

The formula of Equation 4.4.1 is quite general and holds in the case where $N_S/N_W = \mathcal{O}(1)$, so long as we are in the thermodynamic limit, where the energy associated with the interface between S and W may be neglected. In this case, however, one is not licensed to perform the subsequent Taylor expansion, and the distribution P_n is no longer of the Gibbs form. It is also valid for quantum systems⁶, in which case we interpret $P_n = \langle n | \varrho_S | n \rangle$ as a diagonal element of the density matrix ϱ_S . The density of states functions may then be replaced by

$$\begin{aligned} D_W(E_U - E_n) \Delta E &\rightarrow e^{S_W(E_U - E_n, \Delta E)} \equiv \text{Tra}_W \int_{E_U - E_n}^{E_U - E_n + \Delta E} dE \delta(E - \hat{H}_W) \\ D_U(E_U) \Delta E &\rightarrow e^{S_U(E_U, \Delta E)} \equiv \text{Tra}_U \int_{E_U}^{E_U + \Delta E} dE \delta(E - \hat{H}_U) . \end{aligned}$$

The off-diagonal matrix elements of ϱ_S are negligible in the thermodynamic limit.

Averages within the OCE

To compute averages within the OCE,

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\varrho} \hat{A}) = \frac{\sum_n \langle n | \hat{A} | n \rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} , \quad (4.4.13)$$

where we have conveniently taken the trace in a basis of energy eigenstates. In the classical limit, we have

$$\varrho(\varphi) = \frac{1}{Z} e^{-\beta \hat{H}(\varphi)} , \quad Z = \text{Tr} e^{-\beta \hat{H}} = \int d\mu e^{-\beta \hat{H}(\varphi)} , \quad (4.4.14)$$

with $d\mu = \frac{1}{N!} \prod_{j=1}^N (d^d q_j d^d p_j / h^d)$ for identical particles ('Maxwell-Boltzmann statistics'). Thus,

$$\langle A \rangle = \text{Tr}(\varrho A) = \frac{\int d\mu A(\varphi) e^{-\beta \hat{H}(\varphi)}}{\int d\mu e^{-\beta \hat{H}(\varphi)}} . \quad (4.4.15)$$

Entropy and Free Energy

The *Boltzmann entropy* is defined by

$$S = -k_B \text{Tr}(\hat{\varrho} \ln \hat{\varrho}) = -k_B \sum_n P_n \ln P_n . \quad (4.4.16)$$

The Boltzmann entropy and the statistical entropy $S = k_B \ln D(E)$ are identical in the thermodynamic limit. We define the Helmholtz free energy $F(T, V, N)$ as

$$F(T, V, N) = -k_B T \ln Z(T, V, N) , \quad (4.4.17)$$

hence

$$P_n = e^{\beta F} e^{-\beta E_n} , \quad \ln P_n = \beta F - \beta E_n . \quad (4.4.18)$$

Therefore the entropy is

$$S = -k_B \sum_n P_n (\beta F - \beta E_n) \quad (4.4.19)$$

$$= -\frac{F}{T} + \frac{\langle \hat{H} \rangle}{T},$$

which is to say $F = E - TS$, where

$$E = \sum_n P_n E_n = \frac{\text{Tr } \hat{H} e^{-\beta \hat{H}}}{\text{Tr } e^{-\beta \hat{H}}} \quad (4.4.20)$$

is the average energy. We also see that

$$Z = \text{Tr } e^{-\beta \hat{H}} = \sum_n e^{-\beta E_n} \implies E = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = -\frac{\partial}{\partial \beta} \ln Z = \frac{\partial}{\partial \beta} (\beta F). \quad (4.4.21)$$

Thus, $F(T, V, N)$ is a [Legendre transform](#) of $E(S, V, N)$, with

$$dF = -S dT - p dV + \mu dN, \quad (4.4.22)$$

which means

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V}. \quad (4.4.23)$$

Fluctuations in the OCE

In the OCE, the energy is not fixed. It therefore fluctuates about its average value $E = \langle \hat{H} \rangle$. Note that

$$\begin{aligned} -\frac{\partial E}{\partial \beta} &= k_B T^2 \frac{\partial E}{\partial T} = \frac{\partial^2 \ln Z}{\partial \beta^2} \\ &= \frac{\text{Tr } \hat{H}^2 e^{-\beta \hat{H}}}{\text{Tr } e^{-\beta \hat{H}}} - \left(\frac{\text{Tr } \hat{H} e^{-\beta \hat{H}}}{\text{Tr } e^{-\beta \hat{H}}} \right)^2 \\ &= \langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2. \end{aligned}$$

Thus, the heat capacity is related to the fluctuations in the energy, just as we saw at the end of §4:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{1}{k_B T^2} (\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2) \quad (4.4.24)$$

For the nonrelativistic ideal gas, we found $C_V = \frac{d}{2} N k_B$, hence the ratio of RMS fluctuations in the energy to the energy itself is

$$\frac{\sqrt{\langle (\Delta \hat{H})^2 \rangle}}{\langle \hat{H} \rangle} = \frac{\sqrt{k_B T^2 C_V}}{\frac{d}{2} N k_B T} = \sqrt{\frac{2}{Nd}}, \quad (4.4.25)$$

and the ratio of the RMS fluctuations to the mean value vanishes in the thermodynamic limit.

The full distribution function for the energy is

$$P(\mathcal{E}) = \langle \delta(\mathcal{E} - \hat{H}) \rangle = \frac{\text{Tr } \delta(\mathcal{E} - \hat{H}) e^{-\beta \hat{H}}}{\text{Tr } e^{-\beta \hat{H}}} = \frac{1}{Z} D(\mathcal{E}) e^{-\beta \mathcal{E}}. \quad (4.4.26)$$

Thus,

$$P(\mathcal{E}) = \frac{e^{-\beta[\mathcal{E} - TS(\mathcal{E})]}}{\int d\mathcal{E}' e^{-\beta[\mathcal{E}' - TS(\mathcal{E}')]}} \quad (4.4.27)$$

where $S(\mathcal{E}) = k_B \ln D(\mathcal{E})$ is the statistical entropy. Let's write $\mathcal{E} = E + \delta\mathcal{E}$, where E extremizes the combination $\mathcal{E} - T S(\mathcal{E})$, the solution to $T S'(E) = 1$, where the energy derivative of S is performed at fixed volume V and particle number N . We now expand $S(E + \delta\mathcal{E})$ to second order in $\delta\mathcal{E}$, obtaining

$$S(E + \delta\mathcal{E}) = S(E) + \frac{\delta\mathcal{E}}{T} - \frac{(\delta\mathcal{E})^2}{2T^2 C_V} + \dots \quad (4.4.28)$$

Recall that $S''(E) = \frac{\partial}{\partial E} \left(\frac{1}{T} \right) = -\frac{1}{T^2 C_V}$. Thus,

$$\mathcal{E} - T S(\mathcal{E}) = E - T S(E) + \frac{(\delta\mathcal{E})^2}{2T C_V} + \mathcal{O}((\delta\mathcal{E})^3). \quad (4.4.29)$$

Applying this to both numerator and denominator of Equation 4.4.27, we obtain⁷

$$P(\mathcal{E}) = \mathcal{N} \exp \left[-\frac{(\delta\mathcal{E})^2}{2k_B T^2 C_V} \right], \quad (4.4.30)$$

where $\mathcal{N} = (2\pi k_B T^2 C_V)^{-1/2}$ is a normalization constant which guarantees $\int d\mathcal{E} P(\mathcal{E}) = 1$. Once again, we see that the distribution is a Gaussian centered at $\langle \mathcal{E} \rangle = E$, and of width $(\Delta\mathcal{E})_{RMS} = \sqrt{k_B T^2 C_V}$. This is a consequence of the [Central Limit Theorem](#).

Thermodynamics revisited

The average energy within the OCE is

$$E = \sum_n E_n P_n, \quad (4.4.31)$$

and therefore

$$\begin{aligned} dE &= \sum_n E_n dP_n + \sum_n P_n dE_n \\ &= \sum_n E_n dP_n, \end{aligned}$$

where

$$\begin{aligned} \sum_n P_n dE_n &= - \sum_n P_n dE_n \\ \sum_n E_n dP_n &= \sum_n E_n dP_n. \end{aligned}$$

Finally, from $P_n = Z^{-1} e^{-E_n/k_B T}$, we can write

$$E_n = -k_B T \ln Z - k_B T \ln P_n, \quad (4.4.32)$$

with which we obtain

$$\begin{aligned} \sum_n E_n dP_n &= \sum_n E_n dP_n \\ &= -k_B T \ln Z \sum_n dP_n - k_B T \sum_n \ln P_n dP_n \\ &= T d \left(-k_B \sum_n P_n \ln P_n \right) = T dS. \end{aligned}$$

Note also that

$$\mathcal{W} = - \sum_n P_n dE_n \quad (4.4.33)$$

$$= - \sum_n P_n \left(\sum_i \frac{\partial E_n}{\partial X_i} dX_i \right) \quad (4.4.34)$$

$$= - \sum_{n,i} P_n \langle n | \frac{\partial \hat{H}}{\partial X_i} | n \rangle dX_i \equiv \sum_i F_i dX_i, \quad (4.4.35)$$

so the generalized force F_i conjugate to the generalized displacement dX_i is

$$F_i = - \sum_n P_n \frac{\partial E_n}{\partial X_i} = - \left\langle \frac{\partial \hat{H}}{\partial X_i} \right\rangle. \quad (4.4.36)$$

This is the force acting *on* the system⁸. In the chapter on thermodynamics, we defined the generalized force conjugate to X_i as $y_i \equiv -F_i$.

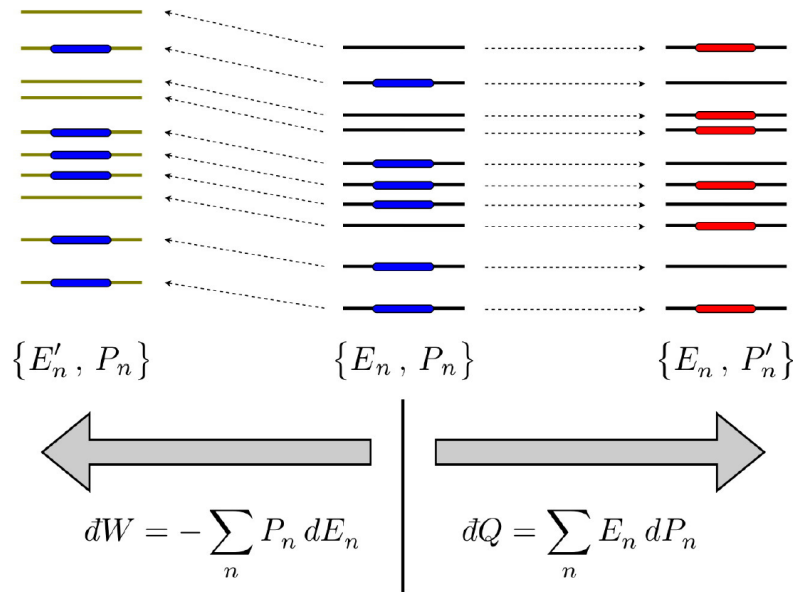


Figure 4.4.1: Microscopic, statistical interpretation of the First Law of Thermodynamics.

Thus we see from Equation ??? that there are two ways that the average energy can change; these are depicted in the sketch of Figure 4.4.1. Starting from a set of energy levels $\{E_n\}$ and probabilities $\{P_n\}$, we can shift the energies to $\{E'_n\}$. The resulting change in energy $(\Delta E)_I = -W$ is identified with the work done *on* the system. We could also modify the probabilities to $\{P'_n\}$ without changing the energies. The energy change in this case is the heat absorbed *by* the system: $(\Delta E)_{II} = Q$. This provides us with a statistical and microscopic interpretation of the First Law of Thermodynamics.

Generalized Susceptibilities

Suppose our Hamiltonian is of the form

$$\hat{H} = \hat{H}(\lambda) = \hat{H}_0 - \lambda \hat{Q}, \quad (4.4.37)$$

where λ is an intensive parameter, such as magnetic field. Then

$$Z(\lambda) = \text{Tr} e^{-\beta(\hat{H}_0 - \lambda \hat{Q})} \quad (4.4.38)$$

and

$$\frac{1}{Z} \frac{\partial Z}{\partial \lambda} = \beta \cdot \frac{1}{Z} \text{Tr} \left(\hat{Q} e^{-\beta \hat{H}(\lambda)} \right) = \beta \langle \hat{Q} \rangle. \quad (4.4.39)$$

But then from $Z = e^{-\beta F}$ we have

$$Q(\lambda, T) = \langle \hat{Q} \rangle = - \left(\frac{\partial F}{\partial \lambda} \right)_T. \quad (4.4.40)$$

Typically we will take Q to be an extensive quantity. We can now define the *susceptibility* χ as

$$\chi = \frac{1}{V} \frac{\partial Q}{\partial \lambda} = - \frac{1}{V} \frac{\partial^2 F}{\partial \lambda^2}. \quad (4.4.41)$$

The volume factor in the denominator ensures that χ is intensive.

It is important to realize that we have assumed here that $[\hat{H}_0, \hat{Q}] = 0$, the ‘bare’ Hamiltonian \hat{H}_0 and the operator \hat{Q} commute. If they do not commute, then the response functions must be computed within a proper quantum mechanical formalism, which we shall not discuss here.

Note also that we can imagine an entire family of observables $\{\hat{Q}_k\}$ satisfying $[\hat{Q}_k, \hat{Q}_{k'}] = 0$ and $[\hat{H}_0, \hat{Q}_k] = 0$, for all k and k' . Then for the Hamiltonian

$$\hat{H}(\vec{\lambda}) = \hat{H}_0 - \sum_k \lambda_k \hat{Q}_k, \quad (4.4.42)$$

we have that

$$Q_k(\vec{\lambda}, T) = \langle \hat{Q}_k \rangle = - \left(\frac{\partial F}{\partial \lambda_k} \right)_{T, N_a, \lambda_{k' \neq k}} \quad (4.4.43)$$

and we may define an entire matrix of susceptibilities,

$$\chi_{kl} = \frac{1}{V} \frac{\partial Q_k}{\partial \lambda_l} = - \frac{1}{V} \frac{\partial^2 F}{\partial \lambda_k \partial \lambda_l}. \quad (4.4.44)$$

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