The Canonical Ensemble

In the microcanonical ensemble, the common thermodynamic variables are \(N\), \(V\), and \(E\). We can think of these as "control" variables that we can "dial in" in order to control the conditions of an experiment (real or hypothetical) that measures a set of properties of particular interest.

However, when we go into the lab, we never "dial in" a particular energy \(E\) for the system. Generally, we can fix external parameters such as temperature \(T\) or pressure \(P\) (or both), but the energy is a quantity to which we simply do not have direct access. For this reason, the microcanonical ensemble is often not the ensemble of choice for performing calculations using statistical mechanics, particularly if one wishes to mimic as closely as possible the conditions of an experiment. In addition, the integral form of the partition function

\[
\Omega (N, V, T) = \dfrac{1}{h^{3N}} \int \limits_{\mathcal{E}(x) = E} dx \label{Eq3.1}
\]

is difficult to use because of the restriction that the mechanical energy \(\mathcal{E}(x)\) be fixed at a chosen value \(E\) for the total internal energy.

The first ensemble we will consider that attempts to capture more closely the conditions of an experiment is the so-called canonical ensemble, which is characterized by the thermodynamic variables \(N\), \(V\), and \(T\). In order to fix the temperature, however, we must have a mechanism to inject heat into the system and extract heat from it in order to regulate the average kinetic energy. This means that the total energy is no longer conserved, as the system must interact with the environment in order to effect this heat exchange.

Conceptually, we imagine that our system interacts with a very large heat source, called a thermal reservoir. The thermal reservoir is also a mechanical system, albeit an extremely large one, with an internal energy \(E_r\) and having \((N_r, V_r)\) particles in a volume \((V_r)\). However, since \((N_r, V_r)\) do not change, we only need to consider how the energy \(E_r\) of the reservoir changes as the energy \(E\) of the system changes. The combination of system \((+1)\) reservoir comprises the thermodynamic universe, which is a microcanonical system (after all, it is isolated from any additional surroundings) having a fixed total energy \(E_T\). Since \((N_r \gg N)\), it follows that \((E_r \ll E)\).

The total energy \((E_T = E + E_r)\). Although \((E_T)\) is fixed, both \((E)\) and \((E_r)\) fluctuate, and this means that the systems are not independent. Thus, if we ask how many microstates are available to the combined system \((+1)\) reservoir, which we will denote \(\mathcal{\Omega}_T (N_T, V_T, E_T)\), where \((N_T = N + N_r)\) and \((V_T = V + V_r)\), we see that we cannot write this as a simple product of \(\mathcal{\Omega}(N, V, E) \mathcal{\Omega}_r (N_r, V_r, E_r)\). In what follows, since \((N), (N_r), (V), \text{and} (V_r)\) never change, we will suppress the dependence of \(\mathcal{\Omega}(E)\) on these and just show the energy dependence. The correct expression for \(\mathcal{\Omega}_T (E_T)\) is

\[
\mathcal{\Omega}_T (E_T) = \int \limits_0^{E_T} \mathcal{\Omega} (E) \mathcal{\Omega}_r (E_T - E) dE \label{Eq3.2}
\]

since \((E_r = E_T - E)\). On the other hand, if we are interested in the number of states available to the system at a particular energy \((E)\), then we can use the simple product formula and write this number, \(\mathcal{\Omega}(E)\), as a ratio:

\[
\mathcal{\Omega} (E) = \dfrac{\mathcal{\Omega}_T (E_T)}{\mathcal{\Omega}_r (E_T - E)} \label{Eq3.3}
\]
The more relevant quantity study is the actual thermodynamic observable, which is the entropy \( S(E) \) of the system. This is given by

\[
\begin{array}{rcl}
S(E) & = & k_B \ln \Omega(E) = k_B \ln \Omega_T(E_T) - k_B \ln \Omega_r(E_T - E) \\
& = & S_T(E_T) - S_r(E_T - E)
\end{array} \label{Eq3.4}
\]

We now exploit the fact that the reservoir is much larger than the system and perform a Taylor expansion up to first order in the system energy. This is justified as \( E \ll E_T \). To first order,

\[
S_r(E_T - E) \approx S_r(E_T) - \left( \frac{\partial S_r}{\partial E_r} \right)_{E_r = E_T} E \label{Eq3.5}
\]

Since \( E_T \) is fixed, and \( E_T = E + E_r \), if the energy of the thermal reservoir change by a small amount \( dE_r \), the system's energy must change by an equal and opposite amount, i.e., \( dE = -dE_r \). Consequently, we can write

\[
S_r(E_T - E) \approx S_r(E_T) + \left( \frac{\partial S_r}{\partial E} \right)_{E_r = E_T} E \label{Eq3.6}
\]

The only thing we still need to do is evaluate the derivative \( \langle \partial S_r/\partial E \rangle \). Thermodynamics posits that heat is a form of energy. If this postulate is correct, then when \( \langle N \rangle \) and \( \langle V \rangle \) remain fixed, any change in energy of the system or reservoir must be due to a transfer of heat \( \langle dQ \rangle \) between the two. Since energy is a state function, how this heat is transferred is irrelevant to the actual energy change we observe, so let us suppose that the transfer is carried out reversibly. Designating the heat transfer as \( \langle dQ_{\text{rev}} \rangle \), the energy change \( \langle dE \rangle \) must equal this heat transfer:

\[
\langle dE = dQ_{\text{rev}} \rangle \label{Eq3.7}
\]

(We will later see that this is in agreement with the first law of thermodynamics.) The thermodynamic definition of entropy then can be used to express \( \langle dQ_{\text{rev}} \rangle \) as

\[
\langle dQ_{\text{rev}} \rangle = TdS_r \label{Eq3.8}
\]

where \( \langle dS_r \rangle \) is the change in entropy of the reservoir as a result of the heat transfer at temperature \( \langle T \rangle \). Rearranging this, we find that the temperature is given by

\[
\langle T \rangle = \left( \frac{\partial S_r}{\partial E} \right)_{N_r, V_r} \label{Eq3.9}
\]

However, since the system and reservoir are in thermal equilibrium, they must have the same temperature. Thus, it follows that

\[
\langle T \rangle = \left( \frac{\partial S}{\partial E} \right)_{N, V} \label{Eq3.10}
\]

Interestingly, we see that we can also use the partition function to determine the temperature

\[
\langle T \rangle = k_B \left( \frac{\partial \ln \Omega}{\partial E} \right)_{N, V} \label{Eq3.11}
\]

which is our first example of how the partition function is used to compute a thermodynamic property! It's also our first illustration of how we start with a purely microscopic description of the system and arrive at a thermodynamic observable.
Now using this relation for temperature in our Taylor expansion, we find

\[ S_r (E_T - E) \approx S_r (E_T) + \frac{E}{T} \quad \text{(Eq3.12)} \]

Therefore,

\[ S(E) = S_T (E_T) - S_r (E_T) - \frac{E}{T} \quad \text{(Eq3.13)} \]

Taking the exponential of both sides, we finally recover the number of states available to the system when it is in contact with a thermal reservoir:

\[ \Omega (E) = e^{S(E)/k_B} = Ce^{-E/k_BT} \quad \text{(Eq3.14)} \]

where \( C \) is a constant.

Of course, what we are really interested in is the number of microstates, as specified by the coordinates and momenta, designated as \( \langle x \rangle \), when the system is in contact with a thermal reservoir. However, Equation \( \langle \text{ref(Eq3.14)} \rangle \) immediately tells us what the probability distribution of \( \langle x \rangle \) needs to be. If we identify the thermodynamic energy \( \langle E \rangle \) with the mechanical energy \( \langle \mathcal{E} (x) \rangle \), then this distribution is given by

\[ f(x) = Ce^{-\mathcal{E}/k_BT} = Ce^{-\beta \mathcal{E} (x)} \quad \text{(Eq3.15)} \]

The mechanical energy is given by

\[
\begin{align}
\mathcal{E} (x) &= \sum_{i=1}^{N} \frac{1}{2} m_i \textbf{v}_i^2 + U(\textbf{r}_1, \ldots, \textbf{r}_N) \\
&= \sum_{i=1}^{N} \frac{\textbf{p}_i^2}{2m_i} + U(\textbf{r}_1, \ldots, \textbf{r}_N)
\end{align} \quad \text{(Eq3.16)}
\]

where the fact that the momentum \( \textbf{p}_i = m_i \textbf{v}_i \) has been used. Written in this way, we also see that the mechanical energy \( \langle \mathcal{E} (x) \rangle \) is also the Hamiltonian \( \langle \mathcal{H} (x) \rangle \). Here, we see that the constant \( C \) can be determined by normalization of the distribution function

\[
\begin{align}
C &= \frac{1}{Q (N, V, T)} \\
Q (N, V, T) &= \frac{1}{h^{3N}} \int e^{-\beta \mathcal{E} (x)}dx = \frac{1}{h^{3N}} \int e^{-\beta \mathcal{H} (x)}dx 
\end{align} \quad \text{(Eq3.17)}
\]

The quantity \( Q (N, V, T) \) is, thus, a measure of the number of microstates available to the system and is, therefore, the partition function of the canonical ensemble. If the \( \langle N \rangle \) particles in the system are all identical, then we need the additional combinatorial factor of \( \langle 1/N! \rangle \) in the definition of \( \langle Q \rangle \), and we write

\[
Q (N, V, T) = \frac{1}{h^{3N}} \int e^{-\beta \mathcal{E} (x)}dx = \frac{1}{h^{3N}} \int e^{-\beta \mathcal{H} (x)}dx 
\]

\[
\text{label(Eq3.18)}
\]

Clearly, there are analogous factors when the system contains \( \langle N_A \rangle \) particles of type \( \langle A \rangle \), \( \langle N_B \rangle \) particles of type \( \langle B \rangle \), and so on.

A few comments are in order at this point. First, we immediately see that if there are no interactions in the system, i.e., \( \langle U = 0 \rangle \), then the canonical distribution function becomes the Maxwell-Boltzmann distribution function.
\[ f(x) = \frac{1}{Q} e^{-\beta \sum_{i=1}^N \frac{m_i \textbf{v}_i^2}{2}} \]  
which is the appropriate canonical distribution for an ideal gas.

A second important point concerns the fact that the energy is a sum of purely momentum-dependent terms and a purely position dependent term:

\[ \mathcal{E}(x) = \sum_{i=1}^N \frac{\textbf{p}_i^2}{2m_i} + U(\textbf{r}_1, \ldots, \textbf{r}_N) \]

Given this, the partition function always separates into a product of two integrals:

\[
\begin{align}
Q(N, V, T) &= C_N \left[ \int e^{-\beta \sum_{i=1}^N \frac{\textbf{p}_i^2}{2m_i}} dx_{\textbf{p}} \right] \left[ \int e^{-\beta U(\textbf{r}_1, \ldots, \textbf{r}_N)} dx_{\textbf{r}} \right] \\
&= C_N \left[ \int e^{-\beta \sum_{i=1}^N \frac{\textbf{p}_i^2}{2m_i}} d\textbf{p}_1 \ldots d\textbf{p}_N \right] \left[ \int e^{-\beta U(\textbf{r}_1, \ldots, \textbf{r}_N)} d\textbf{r}_1 \ldots d\textbf{r}_N \right]
\end{align}
\]

Importantly, note that the first integral is always the same for any system, and in fact, it is just the ideal-gas partition function, which we will work out shortly. The second part, involving the potential energy \(U(\textbf{r}_1, \ldots, \textbf{r}_N)\) is the only part that is different for different systems. In fact, this is the only part of the partition function that is interesting, as it is particular to each individual system and is what gives rise to the particular properties of that system!

A third important point concerns the use of the canonical distribution to compute averages. Let \(\langle A \rangle\) be some equilibrium property of our system, e.g., temperature, pressure, free energy, \(\langle \text{ldots} \rangle\), and let \(\langle a(x) \rangle\) be some function of the coordinates and momenta whose average over an ensemble yields the property \(\langle A \rangle\). An example is the use of the kinetic energy to obtain temperature. In this example, the property \(\langle A \rangle\) is the temperature \(\langle T \rangle\) and the function \(\langle a(x) \rangle\) is the kinetic energy \(a(x) = \frac{2}{3nR} \sum_{i=1}^N \frac{\textbf{p}_i^2}{2m_i}\). The relation between \(\langle A \rangle\) and \(\langle a(x) \rangle\) is

\[
\langle A \rangle = \langle a(x) \rangle \text{rangle} = \int f(x) \: a(x) \: dx = \int e^{\beta \mathcal{E}(x)} \: a(x) \: dx
\]

where \(\langle C_N = 1/h^{3N} \rangle\) if all the particles are distinguishable or \(\langle C_N = 1/N!h^{3N} \rangle\) if they are indistinguishable.

---

**Thermodynamics From the Partition Function**

**Total internal energy**

In the canonical ensemble, the mechanical energy of the system does not conserved but rather fluctuates due to the exchange of heat between it and the thermal reservoir. Thus, if we want to compute the total internal energy, we must perform an average of \(\langle \mathcal{E}(x) \rangle\) over the ensemble. Using the rule in Equation \(\langle \text{ref(Eq3.22)} \rangle\), we would compute the energy as

\[
\langle E \rangle = \int e^{\beta \mathcal{E}(x)} \: dx
\]
Note, however, that we can write

\[ e^\beta \mathcal{E}(x) = -\frac{\partial}{\partial \beta} e^\beta \mathcal{E}(x) \] \label{Eq3.24}\]

Therefore,

\[
\begin{align}
E &= -\frac{C_N}{Q(N, V, T)} \int \frac{\partial}{\partial \beta} e^{-\beta \mathcal{E}(x)} \\
&= -\frac{1}{Q(N, V, T)} \frac{\partial}{\partial \beta} C_N \int e^{-\beta \mathcal{E}(x)} \\
&= -\frac{\partial}{\partial \beta} \ln Q(N, V, T) \label{Eq3.25}\end{align}
\]

Of course, \(Q(N, V, T)\) is as much a function of \(\beta\) as it is a function of \(T\) since \(\beta = \frac{1}{k_B T}\).

### Heat capacity at constant volume

The heat capacity at constant volume, denoted \(C_V\), is defined to be the change in thermodynamic energy with respect to temperature:

\[ C_V = \left( \frac{\partial E}{\partial T} \right)_{N, V} \label{Eq3.26}\]

Since

\[ E = -\frac{\partial}{\partial \beta} \ln Q(N, V, \beta) \label{Eq3.27}\]

we see that

\[
\begin{align}
C_V &= \frac{\partial E}{\partial T} \\
&= \frac{\partial E}{\partial \beta} \frac{\partial \beta}{\partial T} \\
&= \frac{1}{k_B T^2} \frac{\partial^2}{\partial \beta^2} \ln Q(N, V, \beta) \\
&= k_B \beta^2 \frac{\partial^2}{\partial \beta^2} \ln Q(N, V, \beta) \label{Eq3.28}\end{align}
\]

### Pressure

Let us consider a simple thought experiment, which is illustrated in the figure below: A system of \(N\) particles is
FIG. 3.1: Illustration of a thought experiment in which a system is compressed via a piston pushed into the system along the positive \(z\) axis.

Compressed by a piston by pushing the piston in the positive \(z\) direction. Since this is a classical thought experiment, we think in terms of forces. The piston exerts a constant force of magnitude \(F\) on the system. The direction of the force is purely in the positive \(z\) direction, so that we can write the force vector \(\textbf{F}\) as \(\textbf{F} = \begin{pmatrix} 0, 0, F \end{pmatrix}\). The system exerts an equal and opposite force on the piston of the form \(\begin{pmatrix} 0, 0, -F \end{pmatrix}\). If the energy of the system is \(E\), then the force exerted by the system on the piston will be given by the negative change in \(E\) with respect to \(z\):

\[-F = -\frac{dE}{dz} \label{Eq3.29}\]

or

\[F = \frac{dE}{dz} \label{Eq3.30}\]

The force exerted by the system on the piston is manifest as an observable pressure \(P\) equal to the force \(F\) divided by the area \(A\) of the piston, \(P = F/A\). Given this, the observed pressure is just

\[P = \frac{dE}{Adz} \label{Eq3.31}\]

Since the volume decreases when the system is compressed, we see that \(Adz = -dV\). Hence, we can write the pressure as \(P = -dE/dV\).

Of course, the relation \(P = -dE/dV\) is a thermodynamic one, but we need a function of \(x\) that we can average over the ensemble. The most natural choice is

\[p(x) = -\frac{d\mathcal{E}(x)}{dV} \label{Eq3.32}\]

so that \(P = \langle p(x) \rangle\). Setting up the average, we obtain
\[ P = -\frac{C_N}{Q(N, V, T)} \int \frac{\partial \mathcal{E}}{\partial V} e^{-\beta \mathcal{E}(x)} = \frac{C_N}{Q(N, V, T)} \frac{1}{\beta} \int \frac{\partial}{\partial V} e^{-\beta \mathcal{E}(x)} = k_BT \left( \frac{\partial \ln Q(N, V, T)}{\partial V} \right) \]

**Isothermal Compressibility**

Recall from the last problem set that the isothermal compressibility is given by

\[ \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial P}{\partial V} \right)_T^{-1} \]

From Equation \ref{Eq3.33}, we can easily see that the isothermal compressibility can be expressed in terms of the partition function as

\[ \kappa_T = -\frac{1}{Vk_BT} \left( \frac{\partial^2}{\partial V^2} \ln Q(N, V, \beta) \right)^{-1} \]

**Ideal Gas in the Canonical Ensemble**

Recall that the mechanical energy for an ideal gas is

\[ \mathcal{E}(x) = \sum_{i=1}^N \frac{\textbf{p}_i^2}{2m} \]

where all particles are identical and have mass \( m \). Thus, the expression for the canonical partition function \( Q(N, V, T) \):

\[ Q(N, V, T) = \frac{1}{N!h^{3N}} \int dx \: e^{-\beta \sum_{i=1}^N \textbf{p}_i^2/2m} \]

Note that this can be expressed as

\[ Q(N, V, T) = \frac{1}{N!} \left[ \frac{V}{h^3} \left( \frac{2 \pi m}{\beta} \right)^{3/2} \right]^N \]

Evaluating the Gaussian integral gives us the final result immediately:

\[ Q(N, V, T) = \frac{1}{N!} \left( \frac{V}{h^3} \right)^N \left( \frac{2 \pi m}{\beta} \right)^{3N/2} \]

The expressions for the energy

\[ E = -\frac{\partial}{\partial \beta} \ln Q(N, V, T) \]

which give

\[ E = \frac{3}{2}Nk_BT = \frac{3}{2}nRT \]

and pressure
\[ P = k_B T \left( \frac{\partial \ln Q(N, V, T)}{\partial V} \right) \]

give

\[ P = \frac{Nk_BT}{V} = \frac{nRT}{V} \quad \text{label (Eq3.38)} \]

which is the ideal gas law.

Contributors and Attributions

- Mark Tuckerman (New York University)