Relation between $Q_N$ and Helmholtz free energy $A$

\[ A = E - TS \Rightarrow E = A + TS = A - T \left( \frac{\partial A}{\partial T} \right)_{V,N} \]

\[ E = A - T \left( \frac{\partial A}{\partial T} \right)_{V,N} = -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{A}{T} \right) \right]_{V,N} \]

\[ = \left( \frac{\partial (A/T)}{\partial (VT)} \right)_{V,N} = \left( \frac{\partial (\beta A)}{\partial \beta} \right)_{V,N} \]

\[ \Rightarrow E = -\frac{\partial}{\partial \beta} (-\beta A) \]

Compare with \[ \langle E \rangle = -\frac{\partial}{\partial \beta} (\ln Q_N) \]

\[ \Rightarrow A(T,V,N) = -k_B T \ln Q_N(T,V) \]

Another way to write the above is

\[ -\frac{A}{T} = k_B \ln Q_N \]

Note: \(-\frac{A}{T}\) is the Legendre transform of $S$ with respect to $E$

Given \( S(E,V,N) \), \( \left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T} \)

\[ \Rightarrow \text{Legendre transform of } S \text{ with respect to } E \text{ is} \]

\[ S - \frac{E}{T} = \frac{1}{T} (TS - E) = -\frac{A}{T} \]
Now compare

\[-\frac{A}{T} = k_B \ln Q_N\]

\[Q_N\] is canonical partition function

\[S = k_B \ln \Omega\]

\[\Omega\] is microcanonical partition function

the thermodynamic potential is the log of the partition function

\[-\frac{A}{T} = S - \frac{E}{T}\]

\[-\frac{A}{T}\] is Legendre transform of \(S\)

\[Q_N = \int dE \Omega(E) e^{-\beta E}\]

\[Q_N\] is Laplace transform of \(\Omega\)

This holds more generally: If one takes the Laplace transform of a partition function, the corresponding thermodynamic potential of the new partition function is just the Legendre transform of the original thermodynamic potential.

There is still one point to check out more carefully

\[E = -\frac{\partial}{\partial \beta} (-\beta A)\]

is a result within the microcanonical ensemble

where we started with \(S(E,V,N)\) with \(E\) fixed and Legendre transform to get \(A\)

\[\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N\]

is a result within the canonical ensemble with \(E\) fluctuations - only the average \(E\) is fixed by the temperature \(T\).
Alternatively:

\[-\frac{A}{T}\] computed from the Legendre transform of \(S\)

is the \textbf{microcanonical} Helmholtz free energy

\[-\frac{A}{T} = k_B \ln Q_N]\] computed from the canonical partition function \(Q_N\) is the \textbf{canonical} Helmholtz free energy

\[\text{How do we know the two are really the same?}\]

In other words, how do we know that the thermodynamic properties computed within the \textbf{microcanonical ensemble} will agree with the thermodynamic properties computed within the \textbf{canonical ensemble}?

\[\text{How do we know that the two ensembles give equivalent results?}\]

The results will be equivalent if the fluctuations of \(E\) about its average \(\langle E \rangle\) can be ignored.

We will see that this in fact the case in the "thermodynamic limit" of \(N \to \infty\).
Energy fluctuations - In canonical ensemble, $E$ is not fixed, but has a prob dist. How wide is the distr $E$?

Consider

$$\frac{\partial \langle E \rangle}{\partial \beta} = \frac{\partial}{\partial \beta} \left[ \frac{\int dE \, \mathcal{O}(E) e^{-BE}}{Q_N} \right]$$

$$= \frac{\int dE \, E \mathcal{O}(E) e^{-BE}}{Q_N} - \frac{\int dE \, \mathcal{O}(E) e^{-BE}}{Q_N^2} \frac{\partial Q_N}{\partial \beta}$$

$$= -\langle E^2 \rangle - \langle E \rangle \frac{\partial \ln Q_N}{\partial \beta}$$

$$= -\langle E^2 \rangle + \langle E \rangle^2$$

So the fluctuation in the energy $E$ is:

$$\langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial \langle E \rangle}{\partial \beta} = \frac{\partial^2}{\partial \beta^2} (\ln Q_N) = -\frac{2}{\partial \beta} (\beta \mathcal{O}(E))$$

Note: $\langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - 2E\langle E \rangle + \langle E \rangle^2$

$$= \langle E^2 \rangle - 2E\langle E \rangle + \langle E \rangle^2 = \langle E^2 \rangle - \langle E \rangle^2$$

So fluctuation in energy is

$$\langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2 = -\frac{\partial \langle E \rangle}{\partial \beta} = -k_B \frac{\partial \langle E \rangle}{\partial (1/T)} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T}$$

$$= k_B T^2 C_V$$

Specific heat at constant volume

Note: $\langle E \rangle \sim N$, $C_V \sim N$

$$\Rightarrow \sqrt{\frac{\langle E^2 \rangle - \langle E \rangle^2}{\langle E \rangle}} = \sqrt{k_B T^2 C_V} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \to 0 \text{ as } N \to \infty$$
Relation between Canonical and Microcanonical A

We now investigate the effect that the energy fluctuations have on the canonical Helmholtz free energy $A$, as compared to the microcanonical Helmholtz free energy $A_{\text{micro}}$.

**Microcanonical $A$:**

1. Compute $S(E) = k_B \ln S_2(E)$ from the microcanonical partition function $S_2(E)$.
2. Take Legendre transform of $S$ with respect to $E$ to get $A = S - \frac{E}{T}$, this gives the microcanonical $A$.

We will write the Legendre transform as follows:

$$-\frac{A(T)}{T} = \max_E \left[ S(E) - \frac{E}{T} \right]$$

or $A(T) = \min_E \left[ E - TS(E) \right]$

Let $E$ be the minimizing value of $E$.

$$A_{\text{micro}} = E - TS(E)$$

**Canonical $A$:**

1. Compute $A(T) = -k_B T \ln Q_N(T)$.

Consider now the computation of $Q_N = e^{-A/k_B T}$.
\[ Q_N = e^{-A/k_BT} = \int \frac{d\mathcal{E}}{\Delta} e^{-\mathcal{E}/k_BT} \]

\[ = \int \frac{d\mathcal{E}}{\Delta} e^{-\mathcal{E}S(\mathcal{E})/k_BT} \]

\[ = \int \frac{d\mathcal{E}}{\Delta} e^{-(E - TS(\mathcal{E}))/k_BT} \]

Consider the exponent \( E - TS(\mathcal{E}) \) and expand to 2nd order about its minimum at \( E_0 \), \( E = E_0 + \delta E \)

\[ E - TS(\mathcal{E}) = E_0 - TS(E_0) + \delta E - T \left( \frac{\partial^2 S}{\partial \mathcal{E}^2} \right) \delta^2 E - \frac{1}{2} T \left( \frac{\partial (\delta S)}{\partial \mathcal{E}} \right) \delta^2 E \]

1st order 2nd order

\[ = A_{\text{min}} + \delta E - T \left( \frac{1}{T} \right) \delta E - \frac{1}{2} T \left( \frac{\partial^2 (\delta S)}{\partial \mathcal{E}^2} \right) \delta^2 E \]

cancel

\[ = A_{\text{min}} + \frac{1}{2} \left( \frac{\partial T}{\partial \mathcal{E}} \right)_{V,N} \delta^2 E \]

\[ = A_{\text{min}} + \frac{\delta^2 E}{2TC_V} \quad \text{where used} \]

\[ \left( \frac{\partial T}{\partial \mathcal{E}} \right)_{V,N} = \frac{1}{\left( \frac{\partial E}{\partial T} \right)_{V,N}} = \frac{1}{C_V} \]

\[ Q_N = e^{-A/k_BT} = \int \frac{d\mathcal{E}}{\Delta} e^{-A_{\text{min}}/k_BT} \]

\[ - \frac{\delta^2 E}{2k_BT^2C_V} \]

we have a Gaussian integral - integral is sharply peaked at \( \delta E = 0 \) with width \( \sqrt{\langle \delta E^2 \rangle} = \sqrt{k_BT^2C_V} \)

\[ \frac{\sqrt{\langle \delta E^2 \rangle}}{E} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \quad \text{small fluctuations} \]
We can do the Gaussian integration to explicitly evaluate $Q_N$.

\[ Q_N = e^{-\frac{A}{k_B T}} = e^{-\frac{A_{\text{micro}}}{k_B T}} \frac{\sqrt{2\pi k_B T^2 C_V}}{\Delta} \]

Take logs

\[ A = A_{\text{micro}} - k_B T \ln \left( \frac{\sqrt{2\pi k_B T^2 C_V}}{\Delta} \right) \]
\[ A = A_{\text{micro}} - \frac{1}{2} k_B T \ln \left( \frac{2\pi k_B T^2 C_V}{\Delta^2} \right) \]

Canonical \hspace{1cm} \text{microcanonical} \hspace{1cm} \text{correction due to fluctuations in energy}

Helmholtz \hspace{1cm} \text{Helmholtz} \hspace{1cm} \text{free energy} \hspace{1cm} \text{free energy}

Note: $A \sim A_{\text{micro}} \sim N$, \hspace{1cm} $C_V \sim N$

So the correction term between $A$ and $A_{\text{micro}}$ has relative size

\[ \frac{A - A_{\text{micro}}}{A} \sim \frac{\ln N}{N} \to 0 \text{ as } N \to \infty \]
The canonical ensemble gives the same results as the microcanonical ensemble, provided one takes the thermodynamic limit $N \to \infty$.

This is because as $N \to \infty$, the most probable energy $\bar{E}$ is the same as the average energy $\langle E \rangle$, and all other energies have negligible probability to occur.
Note:

\[ Q_N(\beta) = \int_{\Delta} \frac{dE}{\Delta} Q(E) e^{-\beta E} \]

\[ Q_N(\beta) \text{ is Laplace transform of } \frac{Q(E)}{\Delta} \]

\[ \Rightarrow \frac{Q(E)}{\Delta} \text{ is inverse Laplace transform of } Q_N \]

\[ \frac{Q(E)}{\Delta} = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Q_N(\beta) \, d\beta \quad (\beta' > 0) \]

\[ = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\beta' + c\beta'')} Q_N(\beta' + c\beta'') \, d\beta'' \]

where \( \beta' = \text{Re}(\beta) = \alpha' \)

Contour of integration lies to right of imaginary axis.

Entropy \( S = k_B \ln Q \)

Helmholtz \( -\frac{A}{T} = k_B \ln Q_N \)

\[ -\frac{A}{T} = S - \frac{E}{T} \]

Helmholtz free energy is Legendre transform of \( S \) with respect to \( E \)

Thermodynamic potentials which are Legendre transforms of each other, have ensemble partition functions that are Laplace transforms of each other.
Factorization of canonical partition function
- the ideal gas

Consider a system of $N$ noninteracting particles

$$\mathcal{H} \left[ \vec{\mathbf{r}}_j, \vec{p}_j \right] = \sum_{i=1}^{N} \mathcal{H}^{(i)} (\vec{\mathbf{r}}_i, \vec{p}_i)$$

where $\mathcal{H}^{(i)}$ is the single particle Hamiltonian that depends only on the three coordinates $\vec{\mathbf{r}}_i$ and three momenta $\vec{p}_i$ of particle $i$.

$$Q_N = \frac{1}{N! \, \hbar^{3N}} \left( \prod_{i=1}^{N} \int d\vec{\mathbf{r}}_i \, d\vec{p}_i \right) e^{-\beta \mathcal{H}}$$

$$= \frac{1}{N!} \left( \prod_{i=1}^{N} \int d\vec{\mathbf{r}}_i \, d\vec{p}_i \right) e^{-\beta \sum_{j} \mathcal{H}^{(j)} (\vec{\mathbf{r}}_j, \vec{p}_j)}$$

factor the exponential

$$= \frac{1}{N!} \prod_{i=1}^{N} \left( \int d\vec{\mathbf{r}}_i \, d\vec{p}_i \right) e^{-\beta \mathcal{H}^{(i)} (\vec{\mathbf{r}}_i, \vec{p}_i)}$$

factor for particle $i$ is identical to factor for particle $j$

$$\Rightarrow Q_N = \frac{1}{N!} (Q_i)^N$$ for noninteracting particles
where $Q_1$ is the one-particle partition function:

$$Q_1 = \int \frac{d\vec{q}}{\hbar^3} \int d\vec{p} e^{-\beta H^{(1)}(\vec{q}, \vec{p})}$$

Apply to the ideal gas,

$$H^{(1)}(\vec{q}, \vec{p}) = \frac{p^2}{2m}$$

$$Q_1 = \int \frac{d\vec{q}}{\hbar^3} \int d\vec{p} e^{-\beta \frac{p^2}{2m}}$$

$$\int d\vec{q} = V \quad \text{volume of system}$$

$$\int d\vec{p} e^{-\beta \frac{p^2}{2m}} = \left(\frac{2\pi m}{\beta^2}\right)^{3/2} \quad \text{3D Gaussian integral}$$

$$Q_1 = \frac{V}{\hbar^3} \left(2\pi m k_B T\right)^{3/2}$$

$$\Rightarrow Q_N = \frac{1}{N!} \left(\frac{V}{\hbar^3}\right)^N \left(2\pi m k_B T\right)^{3N/2}$$

$$\ln N! = N \ln N - N$$

Using Stirling's formula,

$$A(T,V,N) = -k_B T \ln Q_N$$

$$= -k_B T \left\{ N \ln \left[ \frac{V}{\hbar^3} \left(2\pi m k_B T\right)^{3/2} \right] - N \ln N + N \right\}$$

$$A(T,V,N) = -k_B T N - k_B T N \ln \left[ \frac{V}{\hbar^3 N} \left(2\pi m k_B T\right)^{3/2} \right]$$
Compute average energy

\[ \langle E \rangle = -\frac{2}{3\beta} (\ln AN) = -\frac{2}{3\beta} (-\beta A) \]

\[ = -\frac{2}{3\beta} \left( N + N \ln \left[ \frac{V}{\hbar^3 N} \left( \frac{2\pi m}{\hbar} \right)^{3/2} \right] \right) \]

\[ = -N \frac{2}{3\beta} \left( \ln \beta^{-3/2} \right) = \frac{3}{2} N \frac{2}{3\beta} \ln \beta = \frac{3}{2} N \frac{1}{\beta} \]

\[ \langle E \rangle = \frac{3}{2} N k_B T \quad \text{as expected} \]

Entropy

\[ S = -\left( \frac{\partial A}{\partial T} \right)_{V,N} = k_B N + k_B N \ln \left[ \frac{V}{\hbar^3 N} (2\pi m k_B T)^{3/2} \right] \]

\[ + k_B TN \frac{3}{2} \left( \frac{1}{T} \right) \]

\[ \sim \text{from derivative of log} \]

\[ S = \frac{5}{2} N k_B + k_B N \ln \left[ \frac{V}{\hbar^3 N} (2\pi m k_B T)^{3/2} \right] \]

Substitute in \( k_B T = \frac{2}{3} \frac{E}{N} \) to get

\[ S(E, V, N) = \frac{5}{2} N k_B + k_B N \ln \left[ \frac{V}{\hbar^3 N} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] \]

We have recovered the Sackur-Tetrode equation which we earlier derived from the microcanonical ensemble! Canonical and microcanonical approaches are equivalent.

Because in computing \( AN \) we sum over all states with any energy, as compared to computing \( \Omega \) where we restrict the sum to states in a particular energy shell \( E \), it is usually easier to compute \( AN \), rather than \( \Omega \).
We introduced the canonical distribution as a means of describing a physical system in contact with a heat bath.

The canonical distribution gives the same result as the microcanonical because in the $N \to \infty$ (thermodynamic) limit, the canonical probability distribution

$$P(E) = \frac{\Omega(E) e^{-E/k_B T}}{\Delta \Omega_N(N, T)}$$

approaches a delta-function at the most probable energy = average energy, as set by the temperature $T$.

We could alternatively introduce the canonical ensemble just as a mathematical trick for computing $\Omega(E)$, removing the constraint of constant energy $E$ by means of a Lagrange multiplier.