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 $-\frac{A}{T} = S - \frac{E}{T}$, this gives the microcanonical $A$.

We will write the Legendre transform as follows:

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

or $A(\theta) = \min_{E} \left[ E - TS(E) \right]$

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 $Q_N = e^{-A/k_B T}$
\[ Q_N = e^{-\frac{A}{k_B T}} = \int \frac{dE}{\Delta} S(E) e^{-\frac{E}{k_B T}} \]

Consider the exponent \( E - TS(E) \) ad expand to 2nd order about its minimum at \( E \), \( E = E + \delta E \)

\[ E - TS(E) = \bar{E} - TS(\bar{E}) + \delta E - T \frac{\partial S}{\partial E} \delta E - \frac{1}{2} T \left( \frac{\partial^2 S}{\partial E^2} \right)_{v,N} \delta E^2 \]

\[ = \text{Amiño} + \delta E - T \left( \frac{1}{T} \right) \delta E - \frac{1}{2} T \left( \frac{\partial (TV)}{\partial E} \right)_{v,N} \delta E^2 \]

\[ = \text{Amiño} + \frac{1}{2} \frac{1}{T} \left( \frac{\partial T}{\partial E} \right)_{v,N} \delta E^2 \]

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

\[ \langle \delta E^2 \rangle \sim \frac{1}{N} \sim \frac{1}{\sqrt{N}} \]

small fluctuations
we can do the gaussian integration to explicitly evaluate $Q_N$

\[
\int dx \, e^{-x^2/2 \sigma^2} = \sqrt{2\pi \sigma^2}
\]

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

take logs

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

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

canonical microcanonical correction due to fluctuations in energy

Helmholtz Helmholz free energy free energy

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

so the correction term between $A$ and $A_{\text{micro}}$

has relative size

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

This is because as } N \to \infty, \text{ the most probable energy } \bar{E} \text{ is the same as the average energy } \langle E \rangle, \text{ and all other energies have negligible probability to occur.} \]
Average energy $\langle E \rangle$ vs. the most probable energy $\overline{E}$ in the canonical ensemble.

In our earlier discussion of fluctuations in the canonical ensemble we expanded

$$ E - TS(E) \approx Am(i\omega(T)) + \frac{\delta E^2}{2TCV} $$

now we continue the expansion to $o(\delta E^3)$

$$ E - TS(E) \approx Am(i\omega(T)) + \frac{\delta E^2}{2TCV} + \frac{1}{3!} \left. T \frac{\partial^3 S}{\partial E^3} \right|_{E=\overline{E}} \delta E^3 $$

Note $\frac{\partial^3 S}{\partial E^3} \sim \frac{1}{N^2}$ since $S \sim N$ and $E \sim N$ are both extensive

so we can write

$$ E - TS(E) \approx Am(i\omega(T)) + \frac{\delta E^2}{2TCV} - \frac{\chi \delta E^3}{N^2} $$

where $\chi$ is some constant that does not increase with $N$ (it can depend on $T$)

Now compute $\langle \delta E \rangle = \langle E \rangle - \overline{E}$
\[ \langle SE \rangle = \frac{\int dSE \, e^{-\frac{(E - TS(E))}{k_BT}} \, SE}{\int dSE \, e^{-\frac{(E - TS(E))}{k_BT}}} \]

\[ \approx \frac{\int dSE \, e^{-\frac{SE^2}{2k_BT^2CV} + \frac{SSE^3}{N^2k_BT}} \, SE}{\int dSE \, e^{-\frac{SE^2}{2k_BT^2CV} + \frac{SSE^3}{N^2k_BT}}} \]

where we expanded \( e^{\frac{SSE^3}{N^2k_BT}} \approx 1 + \frac{SSE^3}{N^2k_BT} \)

for \( N \to \infty \)

For a Gaussian distribution, only the even moments are non-vanishing.

\[ \langle SE \rangle \approx \frac{\int dSE \, e^{-\frac{SE^2}{2k_BT^2CV} \left(1 + \frac{SSE^3}{N^2k_BT}\right)} \, SE^4}{\int dSE \, e^{-\frac{SE^2}{2k_BT^2CV}}} \]

\[ = \left(\frac{2}{N^2k_BT}\right) \cdot \left(k_BT^2CV\right)^2 \sum_{n=0}^{\infty} \frac{n^n}{n!} 3 \]
where we used \[ \int_{-\infty}^{\infty} dx \ e^{-\frac{1}{2} \frac{x^2}{\sigma^2}} x^4 \]
\[ \int_{-\infty}^{\infty} dx \ e^{-\frac{1}{2} \frac{x^2}{\sigma^2}} \]
\[ = 3 \sigma^4 \]

But the main point is \[ C_V \sim N \]

so \[ \langle \delta E \rangle \sim \frac{1}{N^2}, N^2 \sim O(1) \]

The relative difference between average and most probable energy therefore scales as

\[ \frac{\langle E \rangle - \bar{E}}{\langle E \rangle} = \frac{\langle \delta E \rangle}{\langle E \rangle} \sim \frac{1}{N} \to 0 \text{ as } N \to \infty \]
Stirling's Formula

In lecture we used the saddle point approx to discuss the relation between the Helmholtz free energy in the canonical vs. the microcanonical ensemble. The saddle pt approx is also how one derives Stirling's approx for \( n! \).

Consider the integral

\[
I = \int_0^\infty dx \, x^n e^{-x}
\]

Integrate by parts

\[
I = -x^n e^{-x} \Big|_0^\infty + \int_0^\infty nx^{n-1} e^{-x} \, dx
\]

Boundary term vanishes at its limits so

\[
I = \int_0^\infty dx \, nx^{n-1} e^{-x}
\]

Integrate by parts again

\[
I = \int_0^\infty dx \, n(n-1)x^{n-2} e^{-x}
\]

and so on to get

\[
I = \int_0^\infty dx \, n(n-1)(n-2) \cdots (1) e^{-x} = n!
\]
Now evaluate $I$ at saddle point approx.

Define $U(x) = -x + n \ln x$

$$I = \int_0^\infty dx \ e^{-U(x)}$$

Expand $U(x)$ about its maximum

$$(U(\bar{x}) = -n + n \ln n$$

$$U'(x) = -1 + \frac{n}{x} \Rightarrow \bar{x} = n \text{ is the maximum}$$

$$U''(x) = -\frac{n}{x^2} \Rightarrow U''(\bar{x}) = -\frac{1}{n}$$

$$U'''(x) = -\frac{2n}{x^3} \Rightarrow U'''(\bar{x}) = -\frac{2}{n^2}$$

$$U''''(x) = -\frac{6n}{x^4} \Rightarrow U''''(\bar{x}) = -\frac{6}{n^3}$$

For $\delta x = x - \bar{x}$,

$$U(x) \approx -n + n \ln n - \frac{\delta x^2}{2n} + \frac{1}{6} \frac{\delta x^3}{n^2} + \frac{1}{24} \frac{\delta x^4}{n^3} + \cdots$$

$$= -n + n \ln n - \frac{\delta x^2}{2n} + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \cdots$$

$$I = \int_0^\infty dx \ e^{-n + n \ln n - \frac{\delta x^2}{2n}} \ e^{-\frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3}} \ e^{\delta x^3 \frac{1}{3n^2} - \delta x^4 \frac{1}{4n^3}}$$

$$\approx \int_{-\infty}^\infty d\delta x \ e^{-n + n \ln n - \frac{\delta x^2}{2n}} \ e^{\delta x^3 \frac{1}{3n^2} - \delta x^4 \frac{1}{4n^3} + o(\delta x^6)}$$

$$= e^{-n + n \ln n} \int_{-\infty}^\infty d\delta x \ e^{-\frac{\delta x^2}{2n}} \ e^{\delta x^3 \frac{1}{3n^2} - \delta x^4 \frac{1}{4n^3} + \cdots}$$

$$= e^{-n + n \ln n} \sqrt{\frac{2\pi n}{\delta}} \left[ 1 + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \cdots \right]$$
Now \( \langle \delta x^3 \rangle = 0 \), \( \langle \delta x^4 \rangle \sim n^2 \), so

\[
I = n! = e^{-n + n \ln n} \sqrt{2\pi n} \left[ 1 + o\left(\frac{1}{n}\right) \right]
\]

\[
\ln n! = n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi + \ln(1 + o\left(\frac{1}{n}\right))
\]

\[
= n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi + o\left(\frac{1}{n}\right)
\]

these are the leading terms

these are next order corrections
Factorization of canonical partition function

**The ideal gas**

Consider a system of $N$ noninteracting particles

$$\mathcal{H}[\mathbf{\bar{q}}, \mathbf{\bar{p}}] = \sum_{i=1}^{N} \mathcal{H}^{(1)}(\mathbf{\bar{q}}_i, \mathbf{\bar{p}}_i)$$

where $\mathcal{H}^{(1)}$ is the single particle Hamiltonian that depends only on the three coordinates $\mathbf{\bar{q}}_i$ and three momenta $\mathbf{\bar{p}}_i$ of particle $i$. 

$$Q_N = \frac{1}{N! \ h^{3N}} \left( \prod_{i=1}^{N} d^{3}q_i \ d^{3}p_i \right) e^{-\beta \mathcal{H}}$$

$$= \frac{1}{N!} \left( \prod_{i=1}^{N} \frac{d^{3}q_i \ d^{3}p_i}{h^3} \right) e^{-\beta \sum \mathcal{H}^{(0)}(\mathbf{\bar{q}}_i, \mathbf{\bar{p}}_i)}$$

$$= \frac{1}{N!} \ \prod_{i=1}^{N} \left( \int d^{3}q_i \ d^{3}p_i \ e^{-\beta \mathcal{H}^{(0)}(\mathbf{\bar{q}}_i, \mathbf{\bar{p}}_i)} \right)$$

\[ \uparrow \]

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

$$Q_N = \frac{1}{N!} (Q_1)^N \text{ for noninteracting particles}$$
where $Q_1$ is the one-particle partition function $Q_1 = \int \frac{d\vec{q}}{h^3} \frac{d\vec{p}}{h^3} e^{-\beta H^{(1)}(\vec{q}, \vec{p})}$

Apply to the ideal gas.

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

\[ Q_1 = \int \frac{d\vec{q}}{h^3} \int \frac{d\vec{p}}{h^3} e^{-\beta \frac{p^2}{2m}} \]

\[ \int d\vec{q} = V \text{ volume of system} \]

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

\[ Q_1 = \frac{V}{h^3} \left( \frac{2\pi m k_B T}{\beta} \right)^{3/2} \]

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

Using Stirling's formula $\ln N! = N \ln N - N$

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

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

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

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

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

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

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

Entropy

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

\[ + k_B N \frac{3}{2} \left( \frac{1}{T} \right) \text{ from derivative of log} \]

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

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

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

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

Because in computing \( Q_N \) we sum over all states with any energy, as opposed to computing \( Q \) where we restrict the sum to states in a particular energy shell \( E \), it is usually easier to compute \( Q_N \), rather than \( Q \).
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.

* Since $E \sim N$ increases as $N \to \infty$ and $\langle E^2 \rangle - \langle E \rangle^2$ increases as $\sqrt{N}$

it is not really $p(E)$ that approaches a well defined function as $N \to \infty$. Rather it is the distribution

$$p(E \equiv E/N)$$

the probability density to have an energy per particle $e$, that approaches a delta function as $N \to \infty$. 
\[ Q_N(\beta) = \int \frac{dE}{A} \Omega(E) e^{-BE} \]

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

\[ \Rightarrow \frac{\Omega}{A} \text{ is inverse Laplace transform of } Q_N \]

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

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

where \( \beta' = \text{Re}(\beta) = 0^+ \)

Contour of integration

leads to right of imaginary axis

Entropy \( S = k_B \ln \Omega \)

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

\[ -\frac{A}{T} = S - \frac{E}{T} \quad \text{(Helmholtz free energy, Legendre transformation of } S \text{ with respect to } E) \]

Thermodynamic potentials, which are Legendre transforms of each other, have ensemble partition functions that are Laplace transforms of each other.
Vital Theorem

Consider \[ \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{\int \exp \left( -\beta H \right) x_i \frac{\partial H}{\partial x_j} \exp \left( -\beta H \right) \, dp_i \, dx_i}{\int \exp \left( -\beta H \right) \exp \left( -\beta H \right) \, dp_i \, dx_i} \]

where \( x_i \) and \( x_j \) are any of the \( 6N \) generalized coordinates \( q, p \), \( i, j = 1, \ldots, 3N \).

\[ \int \exp \left( -\beta H \right) x_i \frac{\partial H}{\partial x_j} \exp \left( -\beta H \right) \, dp_i \, dx_i = \frac{1}{\beta} \int \exp \left( -\beta H \right) x_i \frac{\partial}{\partial x_j} \left( \exp \left( -\beta H \right) \right) \, dp_i \, dx_i \]

Integrate by parts with respect to \( x_j \):

\[ = -\frac{1}{\beta} \int x_j^{(2)} \exp \left( -\beta H \right) \left[ x_j^{(1)} \right] \, dp_i \, dx_i - \frac{1}{\beta} \int \exp \left( -\beta H \right) \frac{\partial}{\partial x_j} \left( x_j \right) \, dp_i \, dx_i \]

The boundary integral vanishes because \( H \) becomes infinite at the extremal values of any coordinate.

- If \( x_j \) is a momentum \( p \), then extremal values are \( p = \pm \infty \) and \( H \propto \pm \infty \rightarrow \infty \).
- If \( x_j \) is a spatial coordinate \( q \), then extremal values are at boundary of system, where the potential energy confining the particle to the volume \( V \) becomes infinite.

\[ \Rightarrow \int \exp \left( -\beta H \right) x_i \frac{\partial H}{\partial x_j} \exp \left( -\beta H \right) \, dp_i \, dx_i = \frac{1}{\beta} \int \exp \left( -\beta H \right) \exp \left( -\beta H \right) \, dp_i \, dx_i \]
but \( \frac{\partial x_i}{\partial x_j} = \delta_{ij} \)

\[
\Rightarrow \quad \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\beta} \delta_{ij} \quad \frac{\int d\mathbf{q}_i \int d\mathbf{p}_i \ e^{-\beta H}}{\int d\mathbf{q}_i \int d\mathbf{p}_i \ e^{-\beta H}}
\]

\[
\langle x_i \frac{\partial H}{\partial x_j} \rangle = k_B T \delta_{ij} \Leftarrow \text{Virial Theorem}
\]

If \( x_i = x_j = p_i \) then

\[
\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \dot{q}_i \rangle = k_B T
\]

If \( x_i = x_j = q_i \), then

\[
\langle q_i \frac{\partial H}{\partial q_i} \rangle = -\langle q_i \dot{p}_i \rangle = k_B T
\]

where we used Hamilton's equations of motion

\[
\frac{\partial H}{\partial p_i} = \dot{q}_i \quad \text{and} \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i
\]

\[
\Rightarrow \quad \left\langle \sum_{i=1}^{3N} p_i \dot{q}_i \right\rangle = 3Nk_B T
\]

\[
-\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3Nk_B T \quad \text{Virial Theorem}
\]

Clausius (1870)
Equation theorem - Classical systems only

Suppose the Hamiltonian is quadratic in some particular degree of freedom \( x_j \) (\( x_j \) is either a coord or a momentum)

\[
\mathcal{H}[\mathbf{q}, \mathbf{p}] = \mathcal{H}'[\mathbf{q}, \mathbf{p}] + \alpha_j x_j^2
\]

depends on all degrees of freedom except \( x_j \)

Then \( \langle \mathcal{H} \rangle = \langle \mathcal{H}' \rangle + \alpha_j \langle x_j^2 \rangle \)

\[\langle x_j^2 \rangle = \frac{\prod_i \int dq_i dp_i \, x_j^2 \, e^{-\beta (\mathcal{H}' + \alpha_j x_j^2)}}{\prod_i \int dq_i dp_i \, e^{-\beta (\mathcal{H}' + \alpha_j x_j^2)}}\]

\[= \left( \prod_i \int dq_i dp_i \, e^{-\beta \mathcal{H}'} \right) \frac{\int dx_j \, x_j^2 \, e^{-\beta \alpha_j x_j^2}}{\left( \prod_i \int dq_i dp_i \, e^{-\beta \mathcal{H}'} \right) \int dx_j \, e^{-\beta \alpha_j x_j^2}}\]

where \( \prod_i \) is over all degrees of freedom except \( x_j \)
\[
\langle x_j^2 \rangle = \frac{\int dx_j x_j^2 e^{-\beta x_j^2}}{\int dx_j e^{-\beta x_j^2}} = \frac{1}{2 \beta a_j} = \frac{1}{2} \frac{k_B T}{a_j}
\]

(follows from \( \int dx e^{-x^2} = \sqrt{\pi} \sigma^2 \) and \( \frac{\int dx e^{-x^2/\sigma^2} x^2}{\sqrt{\pi} \sigma^2} = \sigma^2 \))

So the contribution to \( \langle H \rangle \) from the degree of freedom \( x_j \)

\[
\alpha_j \langle x_j^2 \rangle = \alpha_j \frac{1}{2} \frac{k_B T}{\alpha_j} = \frac{1}{2} k_B T
\]

\( \Rightarrow \) each quadratic degree of freedom in the Hamiltonian contributes \( \frac{1}{2} k_B T \) to the total average energy.

**Ideal gas:** \( H = \sum_{i=1}^{N} \frac{p_i^2}{2m} \)

There are \( 3N \) quadratic degrees of freedom:

the three momenta \( \vec{p}_i \) components for each particle

\( \Rightarrow E = \langle H \rangle = \frac{3N}{2} k_B T \)

or average energy per particle

\( \langle E \rangle = \frac{E}{N} = \frac{3}{2} k_B T \)

as we saw earlier from the single kinetic theory of the ideal gas.