Week 3

Boltzmann Distribution

A system in a large heat reservoir which keeps temperature fixed.

Review

For simplicity, assume energy $U$ is the only macroscopic parameter.

- closed system:

\[ g(U) = \# \text{ states with energy } U \]

\[ P(U) = \frac{1}{g(U)} : \text{ probability for each state.} \]
- 2 systems \( S_1, S_2 \) in thermal contact.

\[
g(u) = \sum_{u_1} g_1(u_1) g_2(u_0-u_1)
\]

- The probability of each state in the combined system is \( \frac{1}{g(u)} \).

- The number of states such that the system \( S_1 \) has energy \( u_1 \) is \( g_1(u_1) \times g_2(u_0-u_1) \).

So, the probability for \( u_1 = 3 \) is

\[
\frac{g_2(u_0-3) \cdot g_1(3)}{g(u)}.
\]

States of \( S_1 \) with \( u_1 = 3 \) are equally probable.
The probability that the system $S_1$ is in a particular state with $V_1 = \omega$, without specifying which state $S_2$ is in, is

\[ P(\omega) = \frac{g_2(V_0 - \omega)}{g(V_0)} \]

This is completely controlled by

\[ g_2(V_0 - \omega) \]

Of course

\[ \sum_\omega g_1(\omega) P(\omega) = 1 \]

\[ P(\omega) \propto g_2(V_0 - \omega) \]
Now suppose $| \delta | \ll | \delta_2 |$

$$\delta$$

heat reservoir

\[ U_0 \sim U_2 \gg U_1 \]

\[ g_2(U_2) \gg g_1(U_1) \]

\[ \sigma_2 = \log g_2(U_2) \]

We can approximate

\[ \sigma_2(U_0 - \delta) \]

\[ \approx \sigma_2(U_0) + (-\delta) \frac{\partial \sigma_2}{\partial U_0} + \ldots \]

\[ \frac{1}{C} = \frac{1}{k_B T} \]
estimate $-\varepsilon$

$$\sigma_2(U_0 - \varepsilon) = \sigma_2(U_0) - \varepsilon \frac{\partial \sigma_2}{\partial U_0}$$

$$+ \frac{1}{2} \varepsilon^2 \frac{\partial^2 \sigma_2}{\partial U_0^2} + \ldots$$

$$\frac{\partial \sigma_2}{\partial U_0} = \frac{1}{c} = \frac{1}{k_B T}$$

$$\frac{\partial^2 \sigma_2}{\partial U_0^2} = - \frac{1}{c^2} \frac{\partial T}{\partial U_0}$$

So, we can ignore $-\varepsilon$ if the reservoir is so large that the temperature does not change much when we change the energy, to the extent $\varepsilon \ll \sigma$. 
Assume this
\[ \sigma_2(U_0 - \varepsilon) = \sigma_2(U_0) - \frac{\varepsilon}{2}. \]

\[ \log g_2(U_0 - \varepsilon). \]

Thus \[ g_2(U_0 - \varepsilon) = g_2(U_0) \cdot e^{-\frac{\varepsilon}{2}}. \]

Let us compute \[ P(\varepsilon) = \frac{g_2(U_0 - \varepsilon)}{g_1(U_0)}. \]

\[ g(U_0) = \sum_{\varepsilon} g_1(\varepsilon) g_2(U_0 - \varepsilon) \]

\[ = g_2(U_0) \sum_{\varepsilon} g_1(\varepsilon) e^{-\frac{\varepsilon}{2}}. \]

Thus \[ P(\varepsilon) = \frac{1}{\sum_{\varepsilon'} g_1(\varepsilon') e^{-\frac{\varepsilon'}{2}}} e^{-\frac{\varepsilon}{2}}. \]
Probability $P(\varepsilon)$

In each state $\varepsilon$ of energy $\varepsilon$ in $\mathcal{S}$,

$$\alpha \propto e^{-\varepsilon/\mathcal{Z}}$$

Boltzmann factor.

Partition function $\mathcal{Z}(\varepsilon)$

$$\mathcal{Z}(\varepsilon) = \sum_\varepsilon g_1(\varepsilon) e^{-\varepsilon/\mathcal{Z}} \quad \text{normalization factor}$$

We can also write

$$\mathcal{Z} = \sum_s e^{-\varepsilon_s/\mathcal{Z}} \quad \text{Energy of state } s$$

The sum over all states in $\mathcal{S}$.

$$\left( \text{Note: } \sum_s \delta\varepsilon, \varepsilon_s = g_1(\varepsilon) \right)$$
When the system $S_1$ is in the heat reservoir at temperature $T$ ($= k_B T$), the probability that $S_1$ is in state $s$ is

$$P(\varepsilon_s) = \frac{1}{Z(T)} e^{-\varepsilon_s / T}.$$ 

(Check:

$$\sum_s P(\varepsilon_s) = \frac{1}{Z} \sum_s e^{-\varepsilon_s / T} = \frac{Z}{Z} = 1$$)

Partition function $Z(T)$ is useful:

$$\langle \varepsilon \rangle = \sum_s \varepsilon_s P(\varepsilon_s) = \frac{1}{Z} \sum_s \varepsilon_s e^{-\varepsilon_s / T} = \frac{1}{Z} \frac{Z'^2}{Z} = \frac{Z'^2}{Z} \log Z(T)$$

$$\langle \varepsilon \rangle = \frac{1}{Z} \frac{Z'^2}{Z} \log Z(T)$$

**Thermal average**
e.g. 2 state system = 8

\[ E_{\text{energy}} = 0 \text{ on } \varepsilon. \]

\[ Z = e^{-\varepsilon/\tau} + e^{-\varepsilon/\tau} = 1 + e^{-\varepsilon/\tau} \]

\[ U \equiv \langle \varepsilon \rangle = \varepsilon \frac{e^{-\varepsilon/\tau}}{1 + e^{-\varepsilon/\tau}} = \frac{\varepsilon}{1 + e^{\varepsilon/\tau}} \]

Compare this with the following

\[ S_1 = 8, \quad S_2 = 8 \otimes N \]

\[ \begin{cases} \mathcal{G}_1(0) = 1 \\ \mathcal{G}_1(\varepsilon) = 1 \end{cases} \quad \mathcal{G}_2(U_2 = M \varepsilon) = \frac{N!}{M! (N-M)!} \]

\( N, M \gg 1 \)

\[ \mathcal{G}_2(U_2 = M \varepsilon) \sim \frac{N^N e^{-N}}{M^M e^{-M} (N-M)^{N-M} e^{-N+M}} \]

\[ = \left( \frac{M}{N} \right)^{-M} \left( 1 - \frac{M}{N} \right)^{-N+M} \]
Set \( U = M \varepsilon \)

\[
\mathcal{G}_2(U) = \left( \frac{U}{N \varepsilon} \right)^{-U/\varepsilon} \left( 1 - \frac{U}{N \varepsilon} \right)^{-N+U/\varepsilon}
\]

\[
\sigma_2(U) = -\frac{U}{\varepsilon} l_{0j} \left( U/N \varepsilon \right)
\]
\[
+ \left( -N + \frac{U}{\varepsilon} \right) l_{0j} \left( 1 - \frac{U}{N \varepsilon} \right)
\]

\[
\frac{1}{\tau} = \frac{\partial \sigma_2}{\partial U} = -\frac{1}{\varepsilon} l_{0j} \left( U/N \varepsilon \right) - \frac{1}{\varepsilon}
\]
\[
+ \frac{1}{\varepsilon} l_{0j} \left( \frac{N \varepsilon - U}{N \varepsilon} \right) + \frac{1}{\varepsilon}
\]

\[
= \frac{1}{\varepsilon} l_{0j} \left( \frac{N \varepsilon}{U} - 1 \right)
\]

\[
= \frac{1}{\varepsilon} l_{0j} \left( \frac{N-M}{M} \right)
\]

**Note** \( \tau = \infty \) at \( M = \frac{1}{2} N \)
The system is unstable when $\tau < 0$.

Because $e^{-\Delta / \theta}$, we can extract more and more energy.

Assume $1 \ll M < \frac{N}{2}$
\[
\frac{\partial^2 \sigma_2}{\partial U^2} = \frac{1}{\varepsilon} \frac{\partial}{\partial U} \log \left( \frac{N\varepsilon}{U} - 1 \right)
\]

\[
= -\frac{1}{\varepsilon} \frac{N\varepsilon}{U^2} \frac{1}{N\varepsilon - U} - 1
\]

\[
= -\frac{1}{\varepsilon^2 M} \frac{1}{N - M}
\]

\[
\sim -\frac{1}{\varepsilon^2 M} \frac{1}{1} \quad \text{suppressed by } \frac{1}{M}.
\]

This is typical:

\[
U, \ \sigma_2: \text{extensive} \sim M, N
\]

\[
\zeta: \text{intensive} \sim 1
\]

\[
\frac{\partial^2 \sigma_2}{\partial U^2} \sim \frac{1}{M} \rightarrow 0.
\]
Helmholtz Free Energy:

\[ \langle \mathcal{E} \rangle = T^2 \frac{\partial}{\partial T} \log Z(T) \]

\[ Z(T) = \sum_{\mathcal{E}} e^{-\mathcal{E}/T} \]

The temperature is defined by

\[ \frac{1}{T} = \frac{\partial \sigma(\mathcal{E})}{\partial \mathcal{E}} \]

\[ \sigma(\mathcal{E}) = \log g(\mathcal{E}) \]

Let us write \( U = \langle \mathcal{E} \rangle \).

If the fluctuation of \( \mathcal{E} \) is small, we can say

\[ \sigma(\langle \mathcal{E} \rangle) = \sigma(0) \langle \mathcal{E} \rangle = \sigma(U) \]
So, we have

\[ U = \tau^2 \frac{2}{\tau} \log Z(\tau) \]

\[ \frac{1}{\tau} = \frac{2}{\partial U} \sigma(U) \]

Now consider

\[ \frac{d}{d\tau} \left( \frac{1}{\tau} U(\tau) - \sigma(U(\tau)) \right) \]

\[ = -\frac{1}{\tau^2} U + \frac{1}{\tau} \frac{dU}{d\tau} - \frac{\partial \sigma}{\partial U} \frac{dU}{d\tau} \]

\[ = -\frac{1}{\tau^2} U = -\frac{2}{\tau} \log Z(\tau) \]

Thus

\[ \frac{1}{\tau} U - \sigma = -\log Z + \text{const.} \]
cost can be included in the normalization of $Z$.

Define $F(\tau) \equiv -\tau \log Z(\tau)$

Then $U - \tau \sigma = F$

**Helmholtz free energy**.

$$\sigma(\varepsilon) \rightarrow \frac{U}{\tau} - \sigma = \frac{1}{\tau} F(\tau)$$

It is called the Legendre transformation.

It is an approximation to the Laplace transformation.
Laplace transform v.s. Legendre transform

\[ f(x) : \text{function of } x \]

\[ \rightarrow e^{g(x)} = \int dx \ e^{-xg} + f(x) \]

Laplace transform: \( e^{f(x)} \rightarrow e^{g(x)} \)

When we can use the steepest descent:

\[ \sim e^{-xg} + f(x) \bigg|_{x: \text{extremum}} \]

\[ g = \frac{df}{dx} \]

In this approximation

\[ g(g) = -xg + f(x), \]

\[ y = \frac{df}{dx} \quad \text{Legendre transform} \]
In our case \( x = \varepsilon \)

\[
f(\varepsilon) = \log g(\varepsilon)
\]

\[
y = \frac{\partial \sigma}{\partial \varepsilon} = \frac{1}{\tau}
\]

So we are looking at

\[
-\frac{1}{\tau} \varepsilon + \sigma(\varepsilon)
\]

On the other hand

\[
\int dx \ e^{-xy + f(x)}
\]

\[
\Rightarrow \int d\varepsilon \ g(\varepsilon) \ e^{-\frac{\varepsilon}{\tau}} = Z(\tau)
\]

Thus \( g(\varepsilon) \rightarrow \log Z(\tau) \)
Thus the relation

\[ F = -\tau \log Z \]

\[ = U - \tau S \]

is the steepest descent approximate to the definition of \( Z \):

\[ Z(z) = \sum_{\xi} g(z) \exp\left(-\frac{\xi}{\tau}\right) \]

Laplace
Pressure

The same story as in the case of temperature. Introduce volume dependence \( V \).

\[ g(\varepsilon, V) \]

\[ 0 (\varepsilon, V) = \log g(\varepsilon, V) \]

Now \( \frac{1}{T} = \left( \frac{\partial \sigma}{\partial \varepsilon} \right) \)

So that

\[ T_1 = T_2 \text{ when } g_1 g_2 \text{ is maximized.} \]

When \( \sigma \) is \( g_1(\varepsilon_1, \nu_1) g_2(\varepsilon_2, \nu_2) \)

maximized keeping \( \nu_1 + \nu_2 = V \) ?

\[ \left( \frac{\partial \sigma_1}{\partial \nu_1} \right)_{\varepsilon_1} = \left( \frac{\partial \sigma_2}{\partial \nu_2} \right)_{\varepsilon_2} \]
This leads to the definition of pressure $P = \left( \frac{\partial \sigma}{\partial \nu} \right)_\varepsilon$.

How to remember signs:

We want $T, \ p > 0$.

$\sigma$ increases as $\varepsilon, \ \nu$ are increased. \( \Rightarrow \ \frac{1}{T} = \frac{\partial \sigma}{\partial \varepsilon} \) $\nu$.

\[
\frac{p}{T} = \left( \frac{\partial \sigma}{\partial \nu} \right)_\varepsilon
\]

We can also write this as:

\[
d\sigma = \frac{p}{T} d\nu + \frac{1}{T} d\varepsilon
\]
On

\[ dE = T \, dS - p \, dV \]

\( p \, dV \): When the system changes the volume \( V \rightarrow V + dv \),
this is the amount of work the system does.

So: The system loses its internal energy \( \Delta E \) by

\[-p \, dV.\]
When macroscopic parameters of the system are $E$ and $V$ only, the only other way $E$ changes is by heat transfer.

So: \[ T \, d\sigma = \dot{Q} \]

\[ \text{heat transfer} \]

(Note: There is no such thing as $Q$, whose variation is $\dot{Q}$.)

\[ \sigma = \int \frac{\dot{Q}}{T} \] was the original definition of “thermodynamic entropy”.)
\[ dU = \tau d\sigma - p dV \]

**Helmholtz free energy**

\[ F = U - T\sigma \]

\[ dF = dU - dT\sigma - \tau d\sigma \]

\[ = \tau d\sigma - p dV - dT\sigma \]

\[ = -\sigma d\tau - p dV \]

So \( F \) is naturally a function \( f(\tau, V) \), as it should.

\[ \left( \frac{\partial F}{\partial \tau} \right)_V = -\sigma, \quad \left( \frac{\partial F}{\partial V} \right)_\tau = -p \]
Ideal Gas

\[ 0 \leq x, y, z \leq L \]

Wave Function

\[ \psi = 0 \]

at the walls.

Schrödinger Equation

\[-\frac{\hbar^2}{2m} \nabla^2 \psi = \varepsilon \psi \]
\[ \Psi = A \sin \left( \frac{m_x \pi x}{L} \right) \sin \left( \frac{m_y \pi y}{L} \right) \sin \left( \frac{m_z \pi z}{L} \right) \]

\[ \varepsilon_{\frac{1}{m}} = \frac{\hbar^2}{2M} \left( \frac{\pi}{L} \right)^2 \left( m_x^2 + m_y^2 + m_z^2 \right) \]

1 Particle partition function

\[ Z_1 = \sum_{m_x, m_y, m_z} e^{-\frac{\hbar^2}{2ML^2} \frac{m_x^2 + m_y^2 + m_z^2}{\varepsilon}} \]

If \( \varepsilon \gg \frac{\hbar^2}{ML^2} \)

\[ \Rightarrow \sum_{m} \sim \int \text{d}n \]
In this approximate,

\[ Z_1 = \int_0^\infty \! dm_1 \, dm_2 \, dm_3 \, e^{-\alpha^2 (m_1^2 + m_2^2 + m_3^2)} \]

\[ \alpha^2 = \frac{\hbar^2 \pi^2}{2ML^2} \]

\[ = \left( \frac{\sqrt{\pi}}{2 \alpha} \right)^3 \]

\[ = \frac{L^3}{(2\pi \hbar^2 / Mt)^{3/2}} \]

\[ = m_0 V \]

\[ m_0 = \left( \frac{M \tau}{2\pi \hbar^2} \right)^{3/2} \]
What does $N_0$ mean?

First, the average energy

$$U = \langle E \rangle = \tau^2 \frac{\partial}{\partial \tau} \log Z$$

$$= \tau^2 \frac{\partial}{\partial \tau} \log (\tau^{3/2})$$

$$= \frac{3}{2} \tau$$

$$= \frac{3}{2} k_B T$$

paying attention to 1 particle in a heat bath of temp $T$. 
\[ \langle \mathcal{E} \rangle = \frac{\hbar^2}{2M} \left( \frac{\pi}{L} \right)^2 \langle m_x^2 + m_y^2 + m_z^2 \rangle \]

\[ = \frac{1}{2M} \langle p_x^2 + p_y^2 + p_z^2 \rangle \]

\[ = \frac{M}{2} \langle v_x^2 + v_y^2 + v_z^2 \rangle \]

\[ = \frac{3}{2} T \]

\[ \langle p_x^2 \rangle = MT \quad \quad p_x = \frac{\hbar}{\lambda_x} \]

\[ \langle v_x^2 \rangle = \frac{T}{M} \]

\[ \langle \lambda_x^2 \rangle = \frac{\hbar^2}{MT} \]

\[ \frac{\hbar}{\sqrt{MT}} : \text{ thermal average} \]

\[ \lambda \quad \text{de Broglie wavelength} \]
\[ \bar{n} \approx \frac{\hbar}{\sqrt{M \tau}} \]

\[ \bar{n} q = \left( \frac{\sqrt{M \tau}}{\hbar} \right)^3 \times \frac{1}{(2\pi)^{3/2}} \]

Quantum concentration

Quantum effects become significant when the density of particles becomes comparable to \( \bar{n} q \)