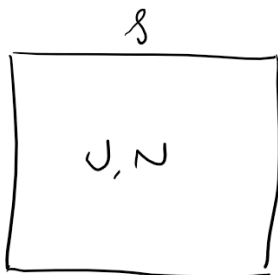


Lecture 7 – Helmholtz free energy

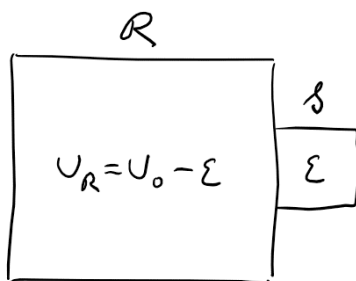
LAST TIME: We've dealt with two statistical ensembles so far



Microcanonical ensemble

System \mathcal{S} is closed so total energy $U_{\mathcal{S}}$ is fixed ($V_{\mathcal{S}}$ also*).

We showed that the entropy $S_{\mathcal{S}}$ increases until it reaches a maximum at equilibrium. $S_{\mathcal{S}}$ is an extremum, i.e. $dS_{\mathcal{S}} = 0$.



Canonical ensemble

System \mathcal{S} is in thermal contact with reservoir \mathcal{R} so temperature $T = T_{\mathcal{S}} = T_{\mathcal{R}}$ is fixed ($V_{\mathcal{S}}$ also*).

$U_0 = U_{\mathcal{S}} + U_{\mathcal{R}}$ is also fixed, but $U_{\mathcal{S}} = E$, $U_{\mathcal{R}}$ can each vary

Total system $\mathcal{R} + \mathcal{S}$ is closed so entropy $S_{\mathcal{R}+\mathcal{S}}$ is an extremum, i.e. $dS_{\mathcal{R}+\mathcal{S}} = 0$.

TODAY: Is there a quantity of the system \mathcal{S} alone that is an extremum? We don't care about \mathcal{R} so we don't want to have to calculate $S_{\mathcal{R}}$!

*Again we consider that N is fixed.

KEY CONCEPT: Helmholtz free energy

Recall the thermodynamic identity. Since $S(U, V)$:

$$dS = \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV = \frac{1}{T} dU + \frac{p}{T} dV$$

if V is fixed

Applying this to the entropy of the total system $\mathcal{R} + \mathcal{S}$:

$$dS_{\mathcal{R}+\mathcal{S}} = 0 = dS_{\mathcal{R}} + dS_{\mathcal{S}}$$

$$\begin{aligned}
&= \frac{dU_{\mathfrak{A}}}{T_{\mathfrak{A}}} + dS_{\mathfrak{S}} \quad \text{but } dU_{\mathfrak{A}} = -dU_{\mathfrak{S}} \text{ since } U_0 = U_{\mathfrak{A}} + U_{\mathfrak{S}} \\
&= -\frac{dU_{\mathfrak{S}}}{T} + dS_{\mathfrak{S}} \quad \text{since } T = T_{\mathfrak{S}} = T_{\mathfrak{A}} \\
&= -\frac{1}{T} d(U_{\mathfrak{S}} - TS_{\mathfrak{S}}) \\
&\quad \uparrow
\end{aligned}$$

This quantity is a property of \mathfrak{S} alone.

Also, if $S_{\mathfrak{A}+\mathfrak{S}}$ is an extremum, so must $U_{\mathfrak{S}} - TS_{\mathfrak{S}}$ be an extremum by this equality.

Define Helmholtz free energy: $F \equiv U - TS$,

such that $dS_{\mathfrak{A}+\mathfrak{S}} = 0$ and $-dF_{\mathfrak{S}} = 0$ at equilibrium.

Notice that $S_{\mathfrak{A}+\mathfrak{S}}$ is a maximum, but $F_{\mathfrak{S}}$ is a minimum, due to $-$ sign.

So, in a canonical ensemble, F of system \mathfrak{S} tends to decrease until it reaches a minimum at equilibrium.

Can we write a thermodynamic identity for F ?

$$\begin{aligned}
dF &= dU - TdS - SdT \\
&= \cancel{TdS} - pdV - \cancel{TdS} - SdT \quad \text{since } dU = TdS - pdV \\
&= -pdV - SdT \\
&= \left(\frac{\partial F}{\partial V} \right)_T dV + \left(\frac{\partial F}{\partial T} \right)_V dT
\end{aligned}$$

Therefore $F = F(T, V)$. Makes sense, canonical ensemble is a constant T , V ensemble. Also,

$$p = -\left(\frac{\partial F}{\partial V} \right)_T \quad \text{and} \quad S = -\left(\frac{\partial F}{\partial T} \right)_V$$

KEY CONCEPT: connection between F and partition function Z

Recall that in microcanonical ensemble, entropy is related to the multiplicity $S_{\mathfrak{S}} = k_B \ln \Omega_{\mathfrak{S}}$.

Because Z is like Ω in counting states for the canonical ensemble, suggests relationship between F and Z .

Propose that $F_{\mathfrak{S}} = -k_B T \ln Z_{\mathfrak{S}}$

Proof. Take the definition of F and its relationship with S :

$$\left(\frac{\partial F}{\partial T}\right)_V = -S = \frac{F - U}{T}$$

Question 1: Prove that the proposed form for F satisfies this differential equation.

Consider the trial function $\tilde{F} = -k_B T \ln Z$ satisfies this differential equation

$$\begin{aligned} \left(\frac{\partial \tilde{F}}{\partial T}\right)_V &= -k_B \ln Z - k_B T \frac{\partial}{\partial T} \ln Z \\ &= -k_B \ln Z + \frac{1}{T} \frac{\partial}{\partial \beta} \ln Z \quad \text{where we use } \frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \\ &= \frac{\tilde{F}}{T} - \frac{U}{T} \end{aligned}$$

So, F and \tilde{F} satisfy the same differential equation. In principle $\tilde{F} = F + \text{const.}$ To show that $\tilde{F} = F$, we need to show that they match for one value of T . Take $T = 0$.

Question 2: Prove that the trial function and F take on the same value at $T = 0$.

$$\tilde{F}(T=0) = -\lim_{T \rightarrow 0} k_B T \ln Z(T) = -\lim_{T \rightarrow 0} k_B T \ln \sum_i e^{-\varepsilon_i / k_B T}$$

As $T \rightarrow 0$, only the first term in Z with lowest energy (i.e. the ground state) will contribute. All other states are frozen out.

$$Z(T \rightarrow 0) = e^{-\varepsilon_0 / k_B T} + e^{-\varepsilon_1 / k_B T} + \dots \approx e^{-\varepsilon_0 / k_B T}$$

so

$$\tilde{F}(T=0) = -\lim_{T \rightarrow 0} k_B T \ln e^{-\varepsilon_0 / k_B T} = \varepsilon_0$$

Compare this to:

$$F(T=0) = U(T=0) = -\frac{\partial}{\partial \beta} \ln Z(T \rightarrow 0) = -\frac{\partial}{\partial \beta} \ln e^{-\beta \varepsilon_0} = \varepsilon_0$$

which matches.

QED

$F = -k_B T \ln Z$ is a very important equation

Now we have simple ways of calculating pressure p and entropy S from Z :

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = k_B T \frac{\partial}{\partial V} \ln Z \quad \text{and} \quad S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial T} k_B T \ln Z$$

Look at ideal monatomic gas $Z = \frac{(n_Q V)^N}{N!}$:

$$\begin{aligned} p &= k_B T \frac{\partial}{\partial V} \ln Z = k_B T \frac{\partial}{\partial V} (\ln V^N + \text{terms independent of } V) \\ &= \frac{N k_B T}{V} \end{aligned}$$

The ideal gas law $pV = N k_B T$.

Now for the entropy:

$$\begin{aligned} S &= \frac{\partial}{\partial T} k_B T \ln Z = k_B \ln Z + k_B T \underbrace{\frac{\partial}{\partial T} \ln Z}_{-F/T} \\ &= k_B \ln \left(\frac{(n_Q V)^N}{N!} \right) + k_B T \frac{\partial}{\partial T} (\ln n_Q^N + \text{terms independent of } T) \end{aligned}$$

Since $n_Q(T) = \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2}$. Also, assume $N \gg 1$ so we can use the Stirling approximation.

$$\begin{aligned} S &= N k_B \ln(n_Q V) - N k_B \ln N + N k_B + k_B T \frac{\partial}{\partial T} (\ln T^{3N/2} + \text{terms independent of } T) \\ &= N k_B \ln \left(\frac{n_Q V}{N} \right) + N k_B + \frac{3}{2} N k_B \\ &= N k_B \left[\ln \left(\frac{n_Q V}{N} \right) + \frac{5}{2} \right] \end{aligned}$$

This is called the Sackur-Tetrode equation

Note: recall that in Lecture 4, we showed that the entropy of an ideal gas should have the form

$$S(U, V) = N k_B \ln V + \frac{3}{2} N k_B \ln U + k_B \ln f(N)$$

Does the Sackur-Tetrode equation agree?

$$\begin{aligned} n_Q(T) &= \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} \quad \text{and} \quad U = \frac{3}{2} N k_B T, \quad \text{so} \quad n_Q = \left(\frac{m U}{3\pi \hbar^2 N} \right)^{3/2} \quad \text{and} \\ S &= N k_B \ln V + \frac{3}{2} N k_B \ln U - \frac{5}{2} N k_B \ln N + \text{const.} \end{aligned}$$

Question 3: Consider a system with two energy levels with energies 0 and Δ . a) Calculate $S(T)$ and b) check that the limits $T = 0$ and ∞ make sense.

The partition function is $Z(T) = 1 + e^{-\beta\Delta}$ so

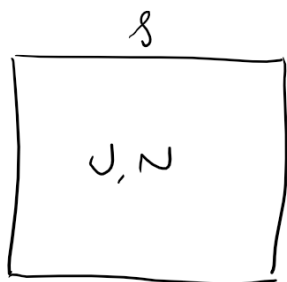
$$S = \frac{\partial}{\partial T} k_B T \ln(1 + e^{-\Delta/k_B T}) = k_B \ln(1 + e^{-\Delta/k_B T}) + \frac{\Delta}{T} \frac{e^{-\Delta/k_B T}}{1 + e^{-\Delta/k_B T}}$$

As $T \rightarrow 0$, $e^{-\Delta/k_B T} \approx 0$ and $S(T \rightarrow 0) = k_B \ln 1 = 0$. Makes sense, only ground state contributes.

As $T \rightarrow \infty$, $e^{-\Delta/k_B T} \approx 1$ and $S(T \rightarrow \infty) = k_B \ln 2$. Makes sense, both states contribute equally.

Before we go further, let's summarize

Microcanonical ensemble



For closed system \mathcal{S} :

Fixed: $U, V(N)$

Extremum: $S = S(U, V)$ (maximum)

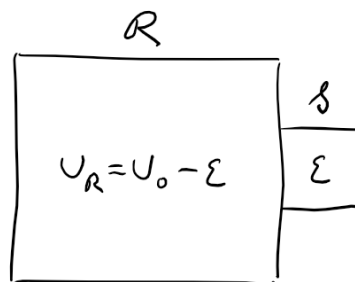
Counting states:

$$\Omega(U) = \sum_{\substack{\text{All states} \\ \text{with energy } U}} 1$$

$$S = k_B \ln \Omega$$

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_T dV \\ &= \frac{1}{T} dU - \frac{p}{T} dV \end{aligned}$$

Canonical ensemble



For system \mathcal{S} in thermal contact with \mathcal{R} :

Fixed: $T, V(N)$

Extremum: $F = F(T, V)$ (minimum)

Counting states:

$$Z(T) = \sum_{\substack{\text{All states} \\ \text{at temperature } T}} e^{-\varepsilon/k_B T}$$

$$F = -k_B T \ln Z$$

$$\begin{aligned} dF &= \left(\frac{\partial F}{\partial T} \right)_V dT + \left(\frac{\partial F}{\partial V} \right)_T dV \\ &= -S dT - p dV \end{aligned}$$

KEY CONCEPT: Gibbs paradox

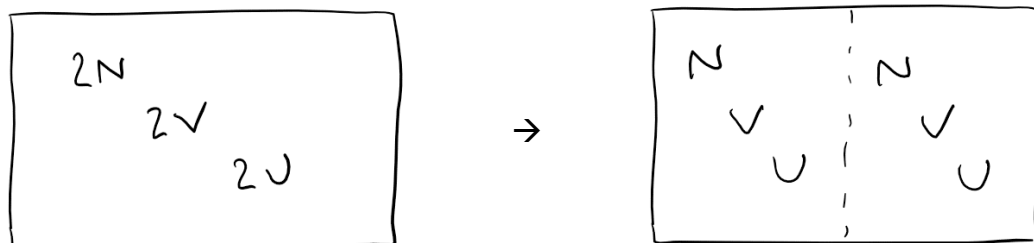
We've encountered $N!$ factor due to indistinguishability of particles. What would happen if we ignored it?

Let's say $Z' = (n_Q V)^N$, then

$$\begin{aligned} S' &= Nk_B \ln n_Q + Nk_B \ln V + \frac{3}{2} Nk_B \\ &= Nk_B \left[\ln(n_Q V) + \frac{3}{2} \right] \\ &= Nk_B \left[\ln \left(\left(\frac{mU}{3\pi\hbar^2 N} \right)^{3/2} V \right) + \frac{3}{2} \right] \end{aligned}$$

What are the consequences?

Consider a closed system consisting of a box of size $2V$ containing an ideal gas of $2N$ identical particles and total energy $2U$.



Imagine introducing a partition so $\frac{1}{2}$ the particles are on one side, $\frac{1}{2}$ on the other.

$$\text{Before: } S'_{\text{before}} = 2Nk_B \left[\ln \left(\left(\frac{m \cancel{2} U}{3\pi\hbar^2 \cancel{2} N} \right)^{3/2} 2V \right) + \frac{3}{2} \right]$$

$$\text{After: } S'_{\text{after}} = 2 \times Nk_B \left[\ln \left(\left(\frac{mU}{3\pi\hbar^2 N} \right)^{3/2} V \right) + \frac{3}{2} \right]$$

So $\Delta S' = S'_{\text{after}} - S'_{\text{before}} = -2Nk_B \ln 2$, which violates the second law!

S' must be incorrect. This is called the Gibbs paradox and is resolved by putting back $N!$

$$S = Nk_B \left[\ln \left(\left(\frac{mU}{3\pi\hbar^2 N} \right)^{3/2} \frac{V}{N} \right) + \frac{5}{2} \right]$$

$$\text{Before: } S_{\text{before}} = 2Nk_B \left[\ln \left(\left(\frac{m\gamma U}{3\pi\hbar^2 \gamma N} \right)^{3/2} \frac{\gamma V}{\gamma N} \right) + \frac{5}{2} \right]$$

$$\text{After: } S_{\text{after}} = 2 \times Nk_B \left[\ln \left(\left(\frac{mU}{3\pi\hbar^2 N} \right)^{3/2} \frac{V}{N} \right) + \frac{5}{2} \right]$$

So $\Delta S = S_{\text{after}} - S_{\text{before}} = 0$, as it should be. Indistinguishability is essential to satisfy the second law.

Notice the form of the (correct) entropy: $S = Nf\left(\frac{U}{N}, \frac{V}{N}\right)$, so $S \rightarrow 2S$ when $N, U, V \rightarrow 2N, 2U, 2V$, i.e. S is extensive.