The energy to do the work comes from two sources — the internal energy of the system, and the flow of heat from the reservoir. Change in free energy reflects the amount of work we can extract as the system is maintained at constant temperature. (Different from adiabatic situation.)

Note that partial derivatives commute.

\[
\frac{\partial}{\partial V} \frac{\partial F}{\partial \tau} = \frac{\partial}{\partial \tau} \frac{\partial F}{\partial V}
\]

Hence

\[
\left( \frac{\partial}{\partial V} \frac{\partial F}{\partial \tau} \right)_V = \left( \frac{\partial}{\partial \tau} \frac{\partial F}{\partial V} \right)_V
\]

An example of a Maxwell relation.

Note: assuming \( Z = \frac{\Sigma e^{-\varepsilon / kT}}{\varepsilon} \)

is dominated by the most probable configuration, as will be the case for a large system, we have

\[
Z \approx e^{-F / kT}
\]

or

\[
F = -kT \log Z
\]
Example: The ideal gas

An application of the partition function. We start with the case of a single atom in a cubic 3-dimensional box with side $L$.

We suppose the particle is completely confined to the box, so we impose the boundary condition $y=0$ on the faces of the cube. The stationary states are

$$\psi(x, y, z) = C \sin(\frac{\pi x L}{x}) \sin(\frac{\pi y L}{x}) \sin(\frac{\pi z L}{x})$$

where $n_x, n_y, n_z$ are positive integers. The energy is

$$H = \frac{-e^2 \nabla^2}{2m} \Rightarrow \Sigma(n_x, n_y, n_z) = \frac{k^2}{2m} \left( \frac{\pi}{L} \right)^2 \left[ n_x^2 + n_y^2 + n_z^2 \right]$$

For a single particle, the partition function is

$$Z_1 = \sum_{n_x, n_y, n_z} e^{-\frac{E}{kT}} = \sum_{n_x, n_y, n_z} \exp \left[ -\frac{E}{2mkT} \left( \frac{\pi}{L} \right)^2 \left( n_x^2 + n_y^2 + n_z^2 \right) \right]$$

Now assume $\alpha = \frac{\frac{L^2 \pi^2}{2m}}{kT} \ll 1$ -- i.e., temperature is large compared to spacing between successive energy levels (which is always true at $T > 0$ for a sufficiently large box $L \rightarrow \infty$). Then the sum may be well approximated by an integral:

$$Z_1 = \int_0^\infty dx dx' dx'' \exp \left[ -\alpha (n_x^2 + n_y^2 + n_z^2) \right]$$

$$\alpha = \frac{\frac{L^2 \pi^2}{2m}}{kT}$$
And \[ \int_0^\infty e^{-ax^2} \, dx = \frac{1}{\sqrt{a}} \int_0^\infty e^{-x^2} \, dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \]
so \[ Z_1 = \left( \frac{1}{2} \sqrt{\frac{\pi}{a}} \right)^3 = \frac{27\sqrt{\pi}}{8} \left( \frac{m_0^2 L^2}{2\pi \hbar^2} \right)^{3/2} \]

\[ Z_1 = n_Q V \]
\[ n_Q = \left( \frac{m_0^2 L^2}{2\pi \hbar^2} \right)^{3/2}, \quad V = L^3 \]

So \( V \) is the volume of the gas, and \( n_Q \) is called the quantum concentration.

It has the dimensions of \( \frac{1}{\text{volume}} \), or

\[ n_Q = \frac{1}{L^3} \quad \text{where} \quad L_Q = \frac{k^2}{m_0} \quad \text{(made from numerical factors of order 1.)} \]

\( L_Q \) is the typical wavelength of a particle in the box with an energy of order the temperature \( T \)

\[ \tau \sim \frac{k^2 L^2}{2m} \]

In converting the sum to an integral in the above derivation, we assumed \( L \gg L_Q \). Under these conditions, quantum effects are not important in determining the equilibrium properties of the particle in the box.

For \( L \gg L_Q \) -- we say that we are in the classical regime.

Now we can use \( Z_1 \) to compute the most probable configuration -- i.e. \( \langle U \rangle \) when the particle is in contact with a reservoir at temperature \( T \).
\[ \langle U \rangle = \frac{2}{3} \frac{\partial}{\partial T} \left( \log Z_1 \right) \]

\[ Z_1 = (\text{const}) \cdot \tau^{3/2} \Rightarrow \log Z_1 = \frac{3}{2} \log \tau + (\tau\text{-independent}) \]

\[ \langle U \rangle = \frac{3}{2} \tau^{1/2} \log \tau = \frac{3}{2} \tau = \frac{3}{2} k_B T \]

For a single particle in a box, we won't have very sharp peaking of the probability distribution about the most probable configuration. But suppose there are \( N \) particles with \( N \gg 1 \). And suppose the particles do not interact with one another: they form an ideal gas.

First suppose that all \( N \) particles are distinguishable — they all carry colors or labels so we can tell them apart. For the ideal gas, the energy is the sum of the energies of the particles:

\[ E = E(1) + E(2) + \cdots + E(N) \]

So the Boltzmann factor becomes

\[ C^{-E/2} = \prod_{i=1}^{N} C^{-E(i)/2} \]

And the sum over states is performed by summing over the quantum states of each particle independently:

\[ Z_N = \prod_{i} \left( \Sigma C^{-E(i)/2} \right) = Z_1^N = \quad \circ \quad (N k_B T)^N \]

From the partition function, we may compute \( U \), pressure \( P \) and entropy \( S \).
\[ U = \frac{3}{2} \frac{\partial F}{\partial \mathcal{Z}} \log \mathcal{Z} \quad F = -2 \log \mathcal{Z} \]

\[ L = -\frac{\partial F}{\partial \mathcal{V}} \quad \mathcal{S} = -\frac{\partial F}{\partial T} \]

Here we have \( \log \mathcal{Z} = N \log(n \sigma V) \)

\[ F = -NT \log(n \sigma V) \]

where \( n \sigma \propto T^{3/2} \)

Hence \[ U_N = \frac{3}{2} N \mathcal{Z} \]

(All the particles contribute \( \frac{3}{2} \mathcal{Z} \) to \( \mathcal{Z} \) energy)

\[ P = -\frac{\partial}{\partial \mathcal{V}} \left(-N \mathcal{T} \log \mathcal{V}\right) \propto \frac{NT}{\mathcal{V}} \]

\[ \Rightarrow PV = NT = Nk_B T \]

The familiar ideal gas law

**Entropy:**

\[ \mathcal{S}_N = -\frac{1}{2} \left(-N \mathcal{T} \log(n \sigma V)\right) \]

\[ \mathcal{S}_N = N \log(n \sigma V) + \frac{3}{2} N \mathcal{Z} \]

(from \( n \sigma \propto T^{3/2} \))

- This is a strange and interesting formula.
- First of all, while formulas for \( U \) and \( P \) are entirely classical, and can be understood with classical reasoning, our formula for \( \mathcal{S} \) depends on \( T \), since

\[ n \sigma = \left(\frac{m \mathcal{Z}}{2\pi k^2}\right)^{3/2} \]

In fact \( n \sigma \) and \( \mathcal{S} \to \infty \) in the \( T \to 0 \) limit
So this entropy is incomprehensible to a classical physicist. We need quantum mechanics to make sense of "counting" the microscopic states of a system.

Secondly -- this formula scales with the number of particles $N$ in a peculiar way. We let $n = N/V$ denote the concentration -- the number of particles per unit volume. Then our formula is

$$\frac{(N)}{N_{\text{total}}} = N \log \left( \frac{n_0}{n} \right) + \frac{3}{2} N + N \log N$$

This term is puzzling -- it does not scale linearly with $N$ (or $V$) when the concentration is held fixed -- entropy does not appear to be extensive in the usual sense. In fact, the $N \log N$ term eventually dominates for a large box.

Our formula does not agree with experiment for real gases...

How do you measure the entropy?

Recall

$$dU = c dt + LdV$$  -- Thermodynamic identity

Heat capacity at constant volume is

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{\partial (25)}{\partial T}$$

How much heat do we need to add to raise the temp. in the box?
(we can test the formula by considering \( C \) instead of \( p \); see p. 167 ff. of text)

It was Gibbs who realized how to fix the formula... we need to regard the atoms as indistinguishable.--- They carry no labels:

\[
\begin{array}{c}
- & \text{orbitals} & B \\
A & \text{orbitals} & -
\end{array}
\]

These two states are really the same.

How do we fix the counting? In the classical regime it is pretty easy. Suppose \( n \ll \mu a \), so \( \delta \gg 1 \).

\[\text{dilute gas} \Rightarrow \# \text{of states} \gg 1 \] and with \( N \) particles, no. of states per particle is large. This means it is not likely that the occupation number of a state is \( > 1 \). So we ignore multiple occupancy in our state counting.

Then our counting for distinguishable particles

\[
\frac{\mu}{A} \frac{\mu}{B} \frac{\mu}{C} \frac{\mu}{D} \frac{\mu}{E}
\]

over counts by a factor of \( N! \).--- see the permutations of the particles leave the state of indistinguishable particles unchanged--- but change the state of particles are distinguishable (assuming no double occupancy) \( \frac{1}{2} \)
Then

$$\ln \left( Z_N \right)_{\text{indist}} = \frac{1}{N!} Z_N$$

or

$$\left( \ln Z_N \right)_{\text{indist}} = \left( \ln Z_N \right)_{\text{dist}} - \ln N!$$

$$\left( F_N \right)_{\text{indist}} = \left( F_N \right)_{\text{dist}} + 2 \ln N!$$

This does not modify $\frac{\partial}{\partial Z} \ln Z$ or $\frac{\partial}{\partial V} E$, so our (successful) predictions for $U$ and $P$ are unmodified — but

$$\left( \overline{F}_N \right)_{\text{indist}} = \left( \overline{F}_N \right)_{\text{dist}} - \ln (N!)$$

And using Stirling: $\ln N! \sim N \ln N - N$

- The crazy $N \ln N$ cancels

$$\left( \overline{F}_N \right)_{\text{indist}} = N \left[ \ln \left( \frac{N!}{n!} \right) + \frac{1}{2} \right]$$

- The Sackur-Tetrode equation

This formula does agree with experiment, and now we obtain $U$ and $P$ in extensive form in $N$ at fixed concentration) — $E$ to dependence remains even in the classical regime.

We'll learn later how to deal with a dense gas, the case in which double occupancy is not unlikely.
Gibbs Free Energy

(\delta W)_{\text{dir}} = N \log (N V) + \frac{1}{2} N \text{ - the naive (wrong) formula}

Let 2 gases at same concentration mix:

\[ \Delta F = (N_1 + N_2) \log (V_1 + V_2) - N_1 \log V_1 - N_2 \log V_2 \]

\[ = N_1 \log \frac{V_1 + V_2}{V_1} + N_2 \log \frac{V_1 + V_2}{V_2} = N \log 2 \text{ for 2 identical boxes} \]

Mixing the gases is irreversible (generates entropy)

This is a correct calculation when two species mix, but not for the case when gas 1 and gas 2 are the same.

Indistinguishability of the particles as a quantum effect with no classical analog.
Entropy of Mixing

Illustrates the competition between minimizing energy and maximizing entropy (quantified by $F = U - TS$) seeks a minimum at specified temperature $T$.

Combine metals A and B by melting them together, and cooling will they crystallize with A and B separated or alloyed together?

Typically, energy favors A's together and B's together. So at zero $T$, they will separate. But entropy favors that they mix.

Suppose $N$ total atoms

$\begin{align*}
&xN \text{ B atoms } x < 1 \\
&(1-x)N \text{ A atoms }
\end{align*}$

At fixed $T$, for $x$ sufficiently small, B atoms will dissolve --- the entropy always wins as $x \to 0$. So, at finite $T > 0$, any metal inevitably contains impurities.

Why --- because here are many ways of placing the B atoms among A atoms.

Let's be more quantitative:
\[ g(N,x) = \frac{N!}{[N(1-x)]!(N_x)!} \]  

- same counting as in our spin model

Now use Stirling

\[ \log N! = N \log N - N + O(1) \]

\[ \log g(N,x) \approx \frac{1}{N_x} \log N \]

\[ \log g(N,x) = 6/N_x \]

\[ = N \log N - N - N(1-x)[\log N + \log(1-x)] + N(1-x) \]

\[ - N \times [\log N + \log x] + N \times \]

\[ = -N \left[ (1-x) \log(1-x) + x \log x \right] \]

(observe \( 0 \leq x \leq 1 \), so both terms are positive)

\[ x \ll 1 \Rightarrow \frac{1}{N_x} \log N \approx -N \times \log x \]

Free energy \( F = U - T S \)

\[ F = \text{constant} + N \left( x + \frac{1}{2} x \log x \right) \]

So for \( T \ll 0 \), atoms want to separate (to minimize \( U \))

\[ \boxed{\text{minimize } U} \]
\[ \frac{dF}{dx} = N \left( e^{-x} + 2 \log x \right) = 0 \]
\[ \Rightarrow \log x = -1 - \frac{e}{x} \]
\[ x = e^{-1} e^{-2/1} \]

As \( x \to 0 \), an exponentially small fraction of \( B \) atoms remain dissolved, in thermal equilibrium.

Our approximation is consistent for \( x \) small, or \( e^{-1/2} < e/2 \), i.e., sufficiently low temp.

Then
\[ F_{\text{min}} = \text{const} + N x_0 \left( e + 2 \log x_0 \right) \]
\[ = \text{const} + N x_0 \left( -2 \right) \]

Actually, differentiation occurs... but a small amount of \( B \) remains dissolved in \( A \) (like iron in a pure crystal!)

\[ \text{Infact} \quad \begin{array}{|c|}
\hline
x_0 & 1 \\
\hline
\end{array} \]

\[ -x \log x - (1-x) \log(1-x) \]
achieves its max at \( x = \frac{1}{2} \), where it has the value \( \log 2 \)

For \( x \to 0 \), the energetic cost becomes insignificant
and \( x \to \frac{1}{2} \). \( \ldots \)

- To make an alloy, you might need to quench to
  stay far from equilibrium
- It is hard on projectiles to make pure materials!