Let us finally solve some problems using ensembles and partition functions, and their connections to thermodynamics.

We will first focus on independent molecules by which is meant that the Hamiltonian of the system of molecules is additive, and the corresponding wavefunction a product:

\[ H = H_a + H_b + H_c + \ldots \quad \psi = \psi_a \psi_b \psi_c \ldots \]

**Distinguishable** molecules

For example, consider a lattice of Argon atoms:

\[
\begin{array}{cccc}
\bullet & \bullet & \bullet & \bullet \\
\bullet & b & c & d
\end{array}
\]

They are distinguishable by their respective positions in the lattice. What is the partition function for independent distinguishable molecules?

\[ Z = \sum_\alpha e^{-\beta E_\alpha} \quad \text{(use index } \alpha \text{ to denote system states)} \]

Let’s say each molecule has 3 energy levels, and there are two molecules. We will use \( \varepsilon_j \) to denote the jth eigenstate of molecule \( a \). Then,

\[ E_\alpha = \varepsilon_j^{(a)} + \varepsilon_k^{(b)} \quad j, k = 1, 2, 3 \]

Now,

\[ Z = z_a z_b \]

since

\[
Z = e^{-\beta (\varepsilon_1^{(a)} + \varepsilon_1^{(b)})} + e^{-\beta (\varepsilon_1^{(a)} + \varepsilon_2^{(b)})} + \ldots + e^{-\beta (\varepsilon_3^{(a)} + \varepsilon_1^{(b)})}
\]

\[
= \left( e^{-\beta \varepsilon_1^{(a)}} + e^{-\beta \varepsilon_2^{(a)}} + e^{-\beta \varepsilon_3^{(a)}} \right) \left( e^{-\beta \varepsilon_1^{(b)}} + e^{-\beta \varepsilon_2^{(b)}} + e^{-\beta \varepsilon_3^{(b)}} \right)
\]

If all are really argon atoms,

\[ Z = q^N \quad \text{independent} \]

\[ \text{distinguishable} \]

What if we have a gas of identical molecules?

The molecules are indistinguishable particles, as they can be anywhere in space.
How would we distinguish between states with energy
\[
\varepsilon_1^{(a)} + \varepsilon_2^{(b)}
\]
and
\[
\varepsilon_2^{(a)} + \varepsilon_1^{(b)}
\]
if both particles are of the same species?

You cannot. So, in the partition function, you must divide by two to not over count the number of system states!

For \(N\) particles, with energy
\[
E_\alpha = \varepsilon_1^{(a)} + \varepsilon_2^{(b)} + \varepsilon_3^{(c)} + \ldots,
\]
divide by \(N!\), the number of arrangements of permuting 1,2,3,... among a,b,c,...

But, what to do about the system state
\[
E_\alpha = \varepsilon_1^{(a)} + \varepsilon_1^{(b)} + \varepsilon_2^{(c)} + \ldots,
\]
where you do not have \(N\) numbers to permute among the \(N\) particles? Then, \(N!\) division wouldn’t be correct. But, if number of available configurations \(\Omega\) is much greater than \(N\) (\(\Omega >> N\)) then the chance of obtaining two molecules in same state, i.e., a configuration where \(\varepsilon_1^{(a)} + \varepsilon_1^{(b)}\), is vanishingly small.

Thus, \(N!\) division is correct for \(\Omega >> N\).

\[
Z = \frac{z}{N!} \quad \text{identical indistinguishable} \quad \Omega >> N
\]

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When is \(\Omega >> N\)? For a particle in box,
\[
\Omega(\varepsilon) = \frac{\pi}{6} \left(\frac{8mL^2\varepsilon}{\hbar^2}\right)^{\frac{3}{2}}, \quad \text{where} \quad \varepsilon = \frac{3}{2} k_B T \quad \text{for the average particle at temperature} \; T.
\]
Combining this with the condition \(\Omega >> N\) leads to
\[
\frac{\pi}{6} \left(\frac{12m\varepsilon}{\hbar^2}\right)^{\frac{3}{2}} \gg \frac{N}{V}
\]
Therefore, Boltzmann behavior is favored by high \(T\), large mass, \(m\), and low density, \(\rho = N/V\).
Probabilities:

**Independent distinguishable:**

\[
p_a = e^{-\beta E_a}/Q = e^{-\beta (\varepsilon_{(a)} + \varepsilon_{(b)} + \ldots)} / \sum_i \sum_j \sum_k \ldots e^{-\beta (\varepsilon_{(a)} + \varepsilon_{(b)} + \ldots)}.
\]

The probability of finding molecule \(a\) in state \(i\) regardless of the state of all the other molecules is

\[
p_i^{(a)} = \frac{\sum_j \sum_k \ldots e^{-\beta \varepsilon_{(a)}(i)}}{\sum_i \sum_k \ldots e^{-\beta \varepsilon_{(b)}}(i)}
\]

Therefore, the probability of finding the “a”th molecule in the ith state is:

\[
p_i = \frac{e^{-\beta \varepsilon_i}}{\sum_j e^{-\beta \varepsilon_j}} \quad \text{independent distinguishable}
\]

**Independent indistinguishable**

The argument is more complicated but the result is the same.

(Note that in this case the question is: what is the probability that any molecule is in state \(i\)?)

To summarize, for independent molecules we can

1) find \(\varepsilon_i\)’s for a given molecule
2) do sums to get \(Z\) for that molecule.
3) get \(Z\) for N molecules.
4) get thermodynamic functions from \(Z\).

**Independent indistinguishable** (ideal gas).

\[
z = \sum_i e^{-\beta \varepsilon_i}
\]

\[
\varepsilon_i = \varepsilon_i^{C.M.} + \varepsilon_i^{rel.}
\]

\[
z = z_{\mu} z_{\text{int}}
\]

“C.M.” denotes center of mass and “rel” denotes relative motion.

\(z_{tr}\) = partition function for translational (C.M.) motion of gas molecule.

\(z_{int}\) = partition function for internal (rel) motion (consists of vibration and rotation).
Translational Partition Function:

A particle of mass $M$ in box of side $L$ has energy states

$$\varepsilon(n_x,n_y,n_z) = \frac{\hbar^2}{8ML^2}(n_x^2 + n_y^2 + n_z^2)$$

The corresponding partition function is

$$z = \sum_{n_x=0}^{\infty} \sum_{n_y=0}^{\infty} \sum_{n_z=0}^{\infty} \exp\left[-\left(\frac{\beta\hbar^2}{8ML^2}(n_x^2 + n_y^2 + n_z^2)\right)\right]$$

$$= \left(\sum_{n=0}^{\infty} e^{-an^2}\right)^3 \text{ where } a = \frac{\beta\hbar^2}{8ML^2}.$$ 

It is hard to do this sum.

But, at $T = 300^\circ\text{K}$, you may work out $a = 10^{-17}$ for $M=$ hydrogen atom mass and take $L = 1 \text{cm}$.

Thus, for $n=1$, exponent is $\exp[-10^{-17}]$, for $n=2$, exponent is $\exp[-10^{-17} \times 4]$.

Clearly, the difference is very, very small. So,

$$\sum_{n=0}^{\infty} e^{-an^2} \approx \int_{0}^{\infty} e^{-an^2} dn = \frac{1}{2} \sqrt{\frac{\pi}{a}}.$$ 

Thus, $z = \left[\frac{2\pi M k_B T}{\hbar^2}\right]^{\frac{1}{2}} V \equiv \frac{V}{\Lambda^3}$; with $V = L^3$ is the container volume.

$\Lambda$ is a length. All partition functions must be dimensionless quantities.

Combining this with $Z = z^N/N!$ yields

$$Z = \frac{1}{N!} \left[\frac{2\pi m k_B T}{\hbar^2}\right]^{\frac{1}{2}N} V^N.$$ 

At this point it is good to recall that:

$$\ln(ab) = \ln(a) + \ln(b)$$

$$\ln a^c = c \ln a$$

Furthermore, when taking derivatives of logs it is simplest to isolate the terms that depend on the variable you are taking the derivative with respect to.
What is $U$?

$$U = k_B T^2 \frac{\partial \ln Z}{\partial T}$$

$$U = k_B T^2 \frac{\partial}{\partial T} \left[ -\ln N! + \frac{3}{2} N \ln T + N \ln \left( \frac{2\pi mk_B}{h^2} \right)^{\frac{3}{2}} \right]$$

Therefore,

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

This is the average (thermodynamic) energy of an ideal gas.

In various places in Levine thermo sections he uses $C_V = 3R/2$ for an ideal monatomic gas. Statistical Thermodynamics provides this result. (Recall that $C_v = \partial U / \partial T$.)

It amounts to each degree of freedom getting $(1/2) k_B T$ of energy on average. There are in three dimensions three degrees of freedom for each of the $N$ molecules (center of mass motion).

What’s $\langle P \rangle \equiv P$?

$$P = k_B T \frac{\partial \ln Z}{\partial V} = N k_B T \frac{\partial \ln z}{\partial V} = \frac{N k_B T}{V},$$

i. e., $PV = N k_B T$ ideal gas. This is where the ideal gas equation of state comes from.

What’s $\langle \mu \rangle = \mu$?

Well, $\mu = G / N$. (In a one-component, one-phase system, the chemical potential is just the Gibbs free energy per particle.)

$$\mu = -k_B T \frac{\partial \ln Z}{\partial N} \quad \text{(Stirling)} \approx -k_B T \ln \left( \frac{z}{N} \right). \quad \ln N! = N \ln N - N$$

From the thermodynamics of the ideal gas, recall that

$$\mu(P,T) = \mu^{(0)}(T) + k_B T \ln P,$$

with $\mu^{(0)}(T)$ the standard state (1 atmosphere) chemical potential.

Comparing thermodynamic and statistical mechanic expressions:
\[ \mu(T, P) = -k_B T \ln \left[ \left( \frac{2\pi M k_B T}{\hbar^2} \right)^{\frac{3}{2}} \frac{V}{N} \right] = -k_B T \ln \left[ \left( \frac{2\pi M k T}{\hbar^2} \right)^{\frac{3}{2}} \frac{k_B T}{P} \right]. \]

(Use ideal gas)

Thus, \( \mu^{(0)}(T) = -k_B T \ln \left[ \left( \frac{2\pi m k T}{\hbar^2} \right)^{\frac{3}{2}} k_B T \right] \).

We have:
1) verified that the standard state is only a function of \( T \).
2) and now have an expression from which \( \mu^{(0)} \) can be found.

Note that the standard state depends on \( h \), Planck's constant – quantum mechanics is ever present.

IMPORTANT QUALIFICATION: The above results are still classical (versus quantum) in the sense that they rely on the difference in the energy levels being small compared with \( k_B T \). This is a general feature. It let us convert a sum to an integral, which was convenient, but also limits the results.

Rotational Partition Function:

Let us first do a heteronuclear diatomic. The energy states are

\[ \varepsilon_j = \frac{J (J + 1) \hbar^2}{8\pi^2 I_e} \equiv B_e \hbar J (J + 1) \]

Then,

\[ z_{\text{rot}}(T) = \sum_i e^{-\beta \varepsilon_i} = \sum_j (2J + 1) e^{-\beta B_e \hbar J (J + 1)} = \sum_j (2J + 1) e^{-J(J+1)\theta_{\text{rot}}/T} \]

\[ \theta_{\text{rot}} = \hbar B_e / k \text{ (units of degrees Kelvin)} \]

Some typical values are: \( \theta_{\text{rot}} = 85.4 \ 2.86 \ 9.0 \ 0.054 \)

The level spacing, \( \Delta \varepsilon \approx \frac{\theta_{\text{rot}}}{T} \). If \( \Delta \varepsilon \ll 1 \), then one can replace the sum by an integral, so

\[ z_{\text{rot}} = \int_0^\infty (2J + 1) e^{-J(J+1)\theta_{\text{rot}}/T} dJ. \]

Noting that \( d \left[ J(J+1) \right] = (2J + 1) dJ \), the integral yields

\[ z_{\text{rot}} = \int_0^\infty e^{-\left(\theta_{\text{rot}}/T\right)x} dx = T / \theta_{\text{rot}} \]

Thus \( \frac{z_{\text{rot}}}{T} \) for the high \( T \) limit.
If this is not accurate enough, one can correct the above in a power series in \( \theta / T \).

\[
Z_{\text{rot}} = \frac{T}{\theta_{\text{rot}}} \left[ 1 + \frac{\theta_{\text{rot}}}{3T} + \left( \frac{1}{15} \right) \left( \frac{\theta_{\text{rot}}}{T} \right)^2 + \ldots \right]
\]

For a homonuclear diatomic, and the classical result, one needs to worry about the configurations in space. Again, divide by 2!

\[
Z_{\text{rot}} = \frac{T}{\sigma \theta_{\text{rot}}} \begin{cases} 
\sigma = 1; \text{ hetero} \\
\sigma = 2; \text{ homo}
\end{cases}
\]

**Vibrational Partition Function:**

For a diatomic, in the harmonic oscillator approximation, the energy states are:

\[
\epsilon_n = \left( n + \frac{1}{2} \right) \nu.
\]

Thus,

\[
Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\epsilon_n / kT} = e^{-\nu / 2kT} \sum_{n=0}^{\infty} \left( e^{-\nu / kT} \right)^n
\]

\[
= e^{-\nu / 2kT} \left[ \frac{1}{1 - e^{-\nu / kT}} \right].
\]

In terms of \( \theta_{\text{vib}} \equiv \nu / k \) (in K)

\[
q_{\text{vib}} = \frac{e^{-\theta_{\text{vib}} / 2T}}{1 - e^{-\theta_{\text{vib}} / T}}
\]

Some typical values are: \( \theta_{\text{vib}} \approx 6,210 \quad 3,340 \quad 3,200 \quad 310 \).

Here, one needs the sum instead of an integral. Actually, for many molecules you only need just first term of the sum, i.e. essentially all molecules are in their ground vibrational state. For \( \text{I}_2 \), need a few terms of the sum.
Fraction in any excited-state $f$ is

$$f = \frac{\text{"amount" in excited state}}{\text{"amount" in any state}} = \frac{\text{any state} - \text{ground state}}{\text{any state}}$$

$$f = \frac{z_{\text{vib}} - e^{-\theta_{\text{vib}}/2T}}{z_{\text{vib}}} = e^{-\theta_{\text{vib}}/T}.$$  

For $\theta_{\text{vib}} = 3000, \ T = 300$, find $f = e^{-10}$

**Electronic Partition Function:**

First atoms. Here, $\Delta \varepsilon_{\text{el}} \sim 10^4 \ K$, typically. So, the molecules are usually in the ground electronic state. What about the degeneracy? For closed shell states, $g_{\text{el}} = 1$. For, e.g., Na $2S_{\frac{1}{2}}$ $g_{\text{el}} = 2$ (one unpaired spin).

Sometimes, $\Delta \varepsilon_{\text{el}} \sim$ room temperature. Then you may need, say, two terms in the Partition Function.

Zero of energy convention: Atoms. Use the atomic ground state (electronic)

$$z_{\text{el}} = g_{\text{el}}^{(0)} + g_{\text{el}}^{(1)} e^{-\varepsilon_{\text{el}}^{(0)}/kT} : \varepsilon_{\text{el}}^{(0)} \equiv 0.$$  

For diatomic molecules. Choose zero of energy with reference to the following potential energy surface.

Thus, take $\varepsilon_{\text{el}}^{(0)} = -D_e$

Then,
For \( z_{vib} \), start “counting” at \( \varepsilon = \hbar \nu / 2 \).

Putting it together for diatomics

\[
z(V, T) = z_{vib}(V, T) z_{rot}(T) z_{vib}(T) z_{cl}(T).
\]

Now that we have the various partition functions, let’s get the thermodynamic properties.

We already did some of the translational ones.

\[
A = -kT \ln Z = A_{tr} + A_{rot} + A_{vib} + A_{cl}
\]

(Since \( Z \) is a product the thermodynamic functions are additive over the various contributions).

\[
A_{tr} = -k_B T \ln \left( q_{tr}^N / N! \right)
\]

\[
A_{tr}^{(\text{Stirling})} = -Nk_B T \ln \left[ \frac{2\pi M k_B T}{h^2} \right]^{\frac{3}{2}} V e
\]

\( e \), here, is “exp.”

\[
A_{rot} = -Nk_B T \ln q_{rot} = -Nk_B T \ln \left( \frac{8\pi^2 I}{h^2} kT \right)
\]

\[
A_{vib} = -Nk_B T \ln \left[ \frac{e^{-\frac{\theta_j}{2kT}}}{1 - e^{-\frac{\theta_j}{kT}}} \right]
\]

The \( N! \) is included with \( A_{tr} \) as it is associated with the translational degeneracy.

\[
E_{rot} = k_B T^2 \frac{\partial \ln Z_{rot}}{\partial T} = Nk_B T. \quad (\text{equipartition, from high } T \text{ classical PF})
\]
\[ S_{\text{rot}} = Nk_B \ln (T e / \theta_{\text{rot}}) \]
\[ E_{\text{vib}} = Nk_B \left[ \frac{\theta_v}{2} + \frac{\theta_v}{e^{\theta_v / T} - 1} \right] \]
\[ S_{\text{vib}} = Nk_B \left[ \frac{\theta_v / T}{e^{\theta_v / T} - 1} - \ln \left( 1 - e^{-\theta_v / T} \right) \right] \]
\[ C_{\text{vib}} = \frac{\partial E_{\text{vib}}}{\partial T} \bigg|_V \]

Note that \( E_{\text{vib}} \to Nk_B T \) at high \( T \). This is equipartition again.

\[ A_{el} = -Nk_B T \ln g_{el}^{(0)} - N D_e \]

\[ E_{el} = -N D_e \] This energy is independent of the ground-state degeneracy.

\[ S_{el} = Nk_B \ln g_{el}^{(0)} \] This entropy only depends on the ground-state degeneracy.

**Polyatomic partition function**

Still use \( H = H_{tr} + H_{\text{rot}} + H_{\text{vib}} + H_{el} \)

\[ z_{tr} = \left[ \frac{2 \pi \left( \Sigma m_i \right) kT}{h^2} \right]^{\frac{3}{2}} \]
\[ z_{el} = g_{el}^{(0)} e^{-e_{el}^{(0)}/kT} \] usually 1 term is appropriate

\[ z_{vib} = \prod_i \left[ \frac{e^{-e_v^{(0)}/kT}}{1 - e^{-e_v^{(0)}/kT}} \right] \]
with $\theta_v^{(i)} = h\nu_i/k_B$ \quad $n = 3n - 6(3n - 5)$ for nonlinear (linear) molecules.

The rotational PF $q_{rot}$ is harder to obtain. For an asymmetric rotor, one cannot even write a closed-form energy-level expression. For the classical (high $T$) limit the integral for the PF can be done (see Mayer and Mayer, pgs 193-194) and leads to

$$q_{rot} = \frac{\pi^{\frac{1}{2}}}{\sigma} \left( \frac{T^3}{\theta_A\theta_B\theta_C} \right)^{\frac{1}{2}}$$

with $\theta_A = \hbar^2/8\pi^2 I_A k_B$, etc.

These partition functions can be evaluated more accurately. For example, one can use corrected values of energy levels—vibration-rotation coupling, etc. In this way one can get as close as desired to any experimental determination of, e.g., $C_V$. 