

Reading

K&K chapter 6 and the first half of chapter 7 (the Fermi gas).

The Ideal Gas Again

Using the grand partition function, we've discussed the Fermi-Dirac and Bose-Einstein distributions and their classical—low occupancy—limit, the Maxwell-Boltzmann distribution.

In lecture 7, we considered an ideal gas starting from the partition function. We considered the states of a single particle in a box and we used the Boltzmann factor and the number of such states to calculate the partition function for a single particle in a box. Then we said the partition function for N weakly interacting particles is the product of N single particle partition functions divided by $N!$,

$$Z_N(\tau) = \frac{1}{N!} Z_1^N = \frac{1}{N!} (n_Q V)^N .$$

We introduced the factor of $N!$ to account for the permutations of the N particles among the single particle states forming the overall composite state of the system.

The introduction of this $N!$ factor was something of a “fast one!” We gave a plausible argument for it, but without a formalism that includes the particle number, it's hard to do more. Now that we have the grand partition function we can reconsider the problem.

In addition to cleaning up this detail, we also want to consider how to account for the internal states of the molecules in a gas, the heat and work, etc., required for various processes with an ideal gas, and also we want to consider the absolute entropy and see how the Sackur-Tetrode formula relates to experiment.

The N Particle Problem

The factor of $N!$ in the ideal gas partition function was apparently controversial in the early days of statistical mechanics. In fact, in Schroedinger's book on the subject, he has a chapter called "The N Particle Problem."

I think this is kind of amusing, so let's see what the N particle problem really is.

The free energy with the $N!$ term is

$$\begin{aligned} F_C &= -\tau \log Z, \\ &= -\tau \log((n_Q V)^N / N!), \\ &= -\tau(N \log n_Q + N \log V - N \log N + N), \\ &= -\tau N \log \left[(m\tau/2\pi\hbar^2)^{3/2} (V/N) \right] - \tau N, \end{aligned}$$

where the subscript C denotes the "correct" free energy. Without the $N!$ term, the "incorrect" free energy is

$$\begin{aligned} F_I &= -\tau \log Z, \\ &= -\tau \log(n_Q V)^N, \\ &= -\tau(N \log n_Q + N \log V), \\ &= -\tau N \log \left[(m\tau/2\pi\hbar^2)^{3/2} V \right] \end{aligned}$$

For the entropy, $\sigma = -\partial F/\partial\tau$,

$$\begin{aligned} \sigma_C &= N \log(n_Q V/N) + (3/2)N + N, \\ &= N \left(\log \frac{n_Q V}{N} + \frac{5}{2} \right), \end{aligned}$$

and

$$\begin{aligned} \sigma_I &= N \log(n_Q V) + (3/2)N, \\ &= N \left(\log(n_Q V) + \frac{3}{2} \right). \end{aligned}$$

With a given amount of gas, the change in entropy between an initial and final state is given correctly by either formula,

$$\sigma_{Cf} - \sigma_{Ci} = \sigma_{If} - \sigma_{Ii} = \frac{3}{2}N \log \frac{\tau_f}{\tau_i} + N \log \frac{V_f}{V_i}.$$

But what happens when we change the amount of gas?

Note that N and V are both extensive quantities; the concentration, $n = N/V$, is an intensive quantity. σ_C is proportional to an extensive quantity. On the other hand, σ_I

contains an extensive quantity times the logarithm of an extensive quantity. This means that the (incorrect) entropy is not proportional to the amount of gas we have!

For example, suppose we have two volumes V , each containing N molecules of (the same kind of) gas at temperature τ . Then each has $\sigma_I = N(\log(n_Q V) + 3/2)$, for a total of $2N(\log(n_Q V) + 3/2)$. We can imagine a volume $2V$ divided in half by a removable partition. We start with the partition in place and the entropy as above. We remove the partition. Now we have $2N$ molecules in a volume $2V$. The entropy becomes $\sigma_I = 2N(\log(2n_Q V) + 3/2)$ which exceeds the entropy with the partition in place by $\Delta\sigma_I = 2N \log 2!$ But did anything really change upon removing the partition? What kind of measurements could we make on the gas in either volume to detect whether the partition were in place or not???

Note that the total σ_C is the same before and after the partition is removed.

We might consider the same experiment but performed with two different kinds of molecules, A and B . We start with N molecules of type A on one side of the partition and N molecules of type B on the other side of the partition. Before the partition is removed, we have

$$\sigma_C = N \left(\log \frac{n_{QA} V}{N} + \frac{5}{2} \right) + N \left(\log \frac{n_{QB} V}{N} + \frac{5}{2} \right),$$

where the two kinds of molecules may have different masses and so might have different quantum concentrations. Now we remove the partition. This time we have to wait for equilibrium to be established. We assume that no chemical reactions occur—we are only waiting for the molecules to diffuse so that they are uniformly mixed. Once equilibrium has been established, each molecule occupies single particle states in a volume $2V$ and the entropy is

$$\sigma_C = N \left(\log \frac{2n_{QA} V}{N} + \frac{5}{2} \right) + N \left(\log \frac{2n_{QB} V}{N} + \frac{5}{2} \right),$$

which is $2N \log 2$ greater than the initial entropy. This increase is called the entropy of mixing.

In the experiment with the same gas on both sides of the partition, the incorrect expression for entropy gave an increase which turns out to be the same as the entropy of mixing if we start out with two different gases. This emphasizes the point that the incorrect expression results from over counting the states by treating the molecules as distinguishable.

In the mixing experiment, we can make measurements that tell us whether the partition has been removed. If we sample the gas in one of the volumes and find all the molecules are type A , then we're pretty sure that the partition hasn't been removed! If we find a mixture of type A and type B , then we're pretty sure that it has been removed.

Finally, note that if we go back to the case of the same gas, and *reinsert* the partition,

then σ_I decreases by $2N \log 2$. This is a violation of the second law!

The Ideal Gas From the Grand Partition Function

An ideal gas is the low occupancy limit of non-interacting particles. In this limit, both the Fermi-Dirac and Bose-Einstein distributions become the Maxwell-Boltzmann distribution which is

$$f(\epsilon) = e^{(\mu - \epsilon)/\tau},$$

where $f(\epsilon) \ll 1$ is the average occupancy of a state with energy ϵ . The chemical potential, μ , is found by requiring that the gas have the correct number of molecules,

$$\begin{aligned} N &= \sum_{\text{All states}} e^{(\mu - \epsilon)/\tau}, \\ &= e^{\mu/\tau} \sum_{\text{All states}} e^{-\epsilon/\tau}, \\ &= e^{\mu/\tau} Z_1, \\ &= e^{\mu/\tau} n_Q V, \end{aligned}$$

where Z_1 is the single particle partition function we discussed earlier. Then

$$\mu = \tau \log \frac{n}{n_Q},$$

as we found earlier.

The free energy satisfies

$$\left(\frac{\partial F}{\partial N} \right)_{\tau, V} = \mu(N, \tau, V),$$

so

$$\begin{aligned} F &= \int_0^N \mu(N', \tau, V) dN', \\ &= \int_0^N \tau \log \frac{N'}{n_Q V} dN', \\ &= \tau \int_0^N (\log N' - \log(n_Q V)) dN', \\ &= \tau \left(N' \log N' - N' - N' \log(n_Q V) \right)_0^N, \\ &= N\tau \left(\log \frac{n}{n_Q} - 1 \right). \end{aligned}$$

Of course, this is in agreement with what we had before. The $N!$ factor that we previously inserted by hand, comes about naturally with this method. (It is responsible for the N in the concentration in the logarithm and the -1 within the parentheses.)

As a reminder, the pressure is found from the free energy by

$$p = - \left(\frac{\partial F}{\partial V} \right)_{\tau, N},$$

which gives the ideal gas equation of state

$$p = \frac{N\tau}{V}.$$

The entropy is found by differentiating with respect to the temperature,

$$\sigma = - \left(\frac{\partial F}{\partial \tau} \right)_{V, N},$$

which gives the Sackur-Tetrode expression,

$$\sigma = N \left(\log \frac{n_Q}{n} + \frac{5}{2} \right).$$

The internal energy is most easily found from

$$U = F + \tau\sigma = \frac{3}{2}N\tau.$$

The energy of an ideal gas depends only on the number of particles and the temperature. Since

$$dU = \tau d\sigma - p dV + \mu dN,$$

the change in energy at constant volume and particle number is just $\tau d\sigma$. Then the heat capacity at constant volume is

$$C_V = \tau \left(\frac{\partial \sigma}{\partial \tau} \right)_{V, N},$$

which for the case of an ideal gas is

$$C_V = \frac{3}{2}N = \frac{3}{2}Nk,$$

where the last expression gives the heat capacity in conventional units. The molar specific heat at constant volume is $(3/2)N_0k = (3/2)R$ where R is the gas constant. The heat

capacity at constant pressure can be found by requiring that dV and $d\tau$ be such that p doesn't change.

$$C_p = \tau \left(\frac{\partial \sigma}{\partial \tau} \right)_{p,N} = \left(\frac{\partial U}{\partial \tau} \right)_{p,N} + p \left(\frac{\partial V}{\partial \tau} \right)_{p,N} .$$

Since U depends only on N and τ ,

$$\left(\frac{\partial U}{\partial \tau} \right)_{p,N} = C_V .$$

With the ideal gas equation of state, $V = (N/p)\tau$,

$$p \left(\frac{\partial V}{\partial \tau} \right)_{p,N} = N ,$$

so

$$C_p = C_V + N , \quad \text{or} \quad C_p = C_V + Nk \quad (\text{in conventional units}) .$$

For the molar heat capacities, we have

$$C_p = C_V + R ,$$

and for the ideal monatomic gas, these are

$$C_V = \frac{3}{2}R , \quad \text{and} \quad C_p = \frac{5}{2}R .$$

The ratio of specific heats is usually denoted by γ , which for an ideal monatomic gas is

$$\gamma = \frac{C_p}{C_V} = \frac{5}{3} .$$

Internal Degrees of Freedom

There are several corrections we might make to our treatment of the ideal gas. If we go to high occupancies, our treatment using the Maxwell-Boltzmann distribution is inappropriate and we should start from the Fermi-Dirac or Bose-Einstein distribution directly.

We have ignored the interactions between molecules. This is a good approximation for low density gases, but not so good for higher densities (but these higher densities can still be low enough that the MB distribution applies). We will discuss an approximate treatment of interactions in a few weeks when we discuss phase transitions.

Finally, we have ignored any internal structure of the molecules. We will remedy this omission now. We imagine that each molecule contains several internal states with energies ϵ_{int} . Note that int is understood to be an index over the internal states. There may be states with the same energy and states with differing energies. In our non-interacting model, the external energy is just the kinetic energy due to the translation motion of the center of mass, ϵ_{cm} . Again, cm is to be understood as an index which ranges over all states of motion of the cm. Although we are considering internal energies, we are not considering ionization or dissociation. When a molecule changes its internal state, we assume the number of particles does not change.

Let's consider the grand partition function for a single state of center of mass motion. That is, we're going to consider the grand partition function for single particle states—with internal degrees of freedom—in a box. The energy of the particle is $\epsilon_{\text{cm}} + \epsilon_{\text{int}}$. Then the grand partition function is

$$\begin{aligned} \mathcal{Z} &= 1 + e^{(\mu - \epsilon_{\text{cm}} - \epsilon_{\text{int},1})/\tau} + e^{(\mu - \epsilon_{\text{cm}} - \epsilon_{\text{int},2})/\tau} + \dots \\ &\quad + \text{two particle terms} + \text{three particle terms} + \dots, \\ &= 1 + e^{(\mu - \epsilon_{\text{cm}})/\tau} \sum_{\text{int}} e^{-\epsilon_{\text{int}}/\tau} \\ &\quad + \text{two particle terms} + \text{three particle terms} + \dots, \\ &= 1 + e^{(\mu - \epsilon_{\text{cm}})/\tau} Z_{\text{int}} + \text{two particle terms} + \text{three particle terms} + \dots, \\ &= 1 + e^{(\mu - \epsilon_{\text{cm}})/\tau} Z_{\text{int}} + e^{2(\mu - \epsilon_{\text{cm}})/\tau} \frac{Z_{\text{int}}^2}{2!} + e^{3(\mu - \epsilon_{\text{cm}})/\tau} \frac{Z_{\text{int}}^3}{3!} + \dots, \end{aligned}$$

where Z_{int} is the partition function for the internal states. The above expression is strictly correct only for bosons. For fermions, we would need to be sure that the multiple particle terms have all particles in different states which means that the internal partition functions do not factor as shown above.

However, we really don't need to worry about this because we're going to go to the classical limit where the occupancy is very small. This means we can truncate the sum

above after the second term,

$$\mathcal{Z} = 1 + e^{(\mu - \epsilon_{\text{cm}})/\tau} Z_{\text{int}} .$$

The mean occupancy of the center of mass state, whatever the internal state, is

$$f(\epsilon_{\text{cm}}) = \frac{e^{(\mu - \epsilon_{\text{cm}})/\tau} Z_{\text{int}}}{1 + e^{(\mu - \epsilon_{\text{cm}})/\tau} Z_{\text{int}}} \approx e^{(\mu - \epsilon_{\text{cm}})/\tau} Z_{\text{int}} ,$$

which is just the Maxwell-Boltzmann distribution with an extra factor of the internal partition function, Z_{int} .

Now we should modify our previous expressions to allow for this extra factor of Z_{int} . Recall that we chose the chemical potential to get the correct number of particles. In that calculation, $\exp(\mu/\tau)$ must be replaced by $\exp(\mu/\tau)Z_{\text{int}}$, and everything else will go through as before. Then our new expression for μ is

$$\mu = \tau \log \frac{n}{n_Q Z_{\text{int}}} = \tau \left(\log \frac{n}{n_Q} - \log Z_{\text{int}} \right) .$$

The free energy becomes

$$F = F_{\text{cm}} + F_{\text{int}} = N\tau \left(\log \frac{n}{n_Q Z_{\text{int}}} - 1 \right) ,$$

where F_{cm} is our previous expression for the free energy due to the center of mass motion of molecules with no internal degrees of freedom, and

$$F_{\text{int}} = -N\tau \log Z_{\text{int}} ,$$

is the free energy of the internal states alone. The expression for the pressure is unchanged since in the normal situation, the partition function of the internal states does not depend on the volume. (Is this really true? How do we get liquids and solids? Under what conditions might it be a good approximation?) The expression for the entropy becomes

$$\sigma = \sigma_{\text{cm}} + \sigma_{\text{int}} ,$$

where σ_{cm} is our previous expression for the entropy of an ideal gas, the Sackur-Tetrode expression, and

$$\sigma_{\text{int}} = - \left(\frac{\partial F_{\text{int}}}{\partial \tau} \right)_{V,N} = \left(\frac{\partial (N\tau \log Z_{\text{int}})}{\partial \tau} \right)_{V,N} = N \log Z_{\text{int}} + N\tau \left(\frac{\partial (\log Z_{\text{int}})}{\partial \tau} \right)_{V,N} .$$

The energy, U , and therefore the heat capacities, receive a contribution from the internal states. The extra energy is

$$U_{\text{int}} = F_{\text{int}} + \tau \sigma_{\text{int}} = F_{\text{int}} - \tau \left(\frac{\partial F_{\text{int}}}{\partial \tau} \right)_{V,N} = -\tau^2 \frac{\partial}{\partial \tau} \left(\frac{F_{\text{int}}}{\tau} \right) .$$