1 Week 6: Ideal gas (K&K 6, Schroeder 6.7)

1.1 Midterm on Monday

Topics are everything through week 4, including week 3 homework, which was due in week 4. Problems should be similar to homework problems, but designed to be completed in class. The exam will be closed notes. You should be able to remember the fundamental equations:

$$
\begin{aligned}
dU &= TdS - pdV \tag{1}\\
F &= U - TS \tag{2}\\
dF &= -SdT - pdV \tag{3}\\
P_i &= \frac{e^{-\beta E_i}}{Z} \tag{4}\\
Z &= \sum_i e^{-\beta E_i} \tag{5}\\
U &= \sum_i E_i P_i \tag{6}\\
F &= -kT \ln Z \tag{7}\\
S &= -k \sum_i P_i \ln P_i \tag{8}\\
& \tag{9}
\end{aligned}
$$

If you need a property of a particular system (the ideal gas, the simple harmonic oscillator), it will be given to you. There is no need, for instance, to remember the Stefan-Boltzmann law or the Planck distribution.

1.2 Motivation

You may recall that when we solved for the free energy of an ideal gas, we had a fair amount of work to sum over all possible sets of quantum numbers for each atom, and then to remove the double-counting due to the fact that our atoms were identical. We had a similar issue when dealing with photon modes and blackbody radiation, but in that case one approach was to treat each mode as a separate system, and then just sum over all the modes separately, without ever needing to find the partition function of all the modes taken together.

This week we will be looking at how we can treat each *orbital* (i.e. possible quantum state for a single non-interacting particle) as a separate system (which may or may not be occupied). This can only work when we work in the grand canonical ensemble, but will greatly simplify our understanding of such systems.

1.3 Quantum mechanics and orbitals

Kittel uses the term **orbital** to refer to an energy eigenstate (or wave function) of a one-particle system. How do things differ when we have more than one particle?

Suppose we have three particles (and ignore spin for a moment). The wave function would be written as $\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots)$. This function in general has nothing to do with any single-particle orbitals. Orbitals arise when we consider a Hamiltonian in which there are no interactions between particles:

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + V(\vec{r}_1) + \frac{\hat{p}_2^2}{2m} + V(\vec{r}_2) + \cdots \tag{10}$$

When our Hamiltonian is separable in this way (i.e. the particles don't interact, and there are no terms that involve both $\vec{r}_1$ and $\vec{r}_2$), we can use separation of variables in the solution, and we obtain a wave function that is a product of orbitals:

$$|i_1, i_2, i_3, \cdots\rangle \doteq \phi_{i_1}(\vec{r}_1)\phi_{i_2}(\vec{r}_2)\phi_{i_3}(\vec{r}_3)\cdots \tag{11}$$

Assuming the potential and mass are the same for every particle, these orbitals are eigenstates of the following single-particle eigenvalue equation:

$$\left(\frac{\hat{p}^2}{2m} + V(\vec{r})\right)\phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) \tag{12}$$

There is a catch, however, which arises if the particles are truly indistinguishable (as is the case for electrons, protons, atoms of the same isotope, etc.). In this case, there is a symmetry which means that permuting the labels of our particles cannot change any probabilities:

$$\begin{align}
|\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots)|^2 &= |\Psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \cdots)|^2 \tag{13}\\
&= |\Psi(\vec{r}_2, \vec{r}_3, \vec{r}_1, \cdots)|^2 \tag{14}
\end{align}$$

The simple product we wrote above doesn't have this symmetery, and thus while it is an eigenfunction of our eigenvalue equation, it cannot represent the state of a real system of identical particles. Fortunately, this is pretty easy to resolve: permuting the labels doesn't change the energy, so we have a largish degenerate subspace in which to work. We are simply required to take a linear combination of these product states which *does* have the necessary symmetry.

The above equation, while true, does not tell us what happens to the wave function when we do a permutation, only to its magnitude. As it turns out, there are two types of symmetry possible: bosons and fermions.

1.3.1 Fermions

Fermions are particles with half-integer spin, such as electrons and protons. Fermions are antisymmetric when we exchange the labels of any two particles.

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots) = -\Psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \cdots) \tag{15}$$

This formula is Pauli's exclusion principle.

This isn't a quantum class, so I won't say much more, but we do need to connect with the orbitals picture. When we have non-interacting fermions, their energy eigenstates can be written using a Slater determinant, which is just a convenient way to write the proper antisymmetric linear combination of all possible product states with the same set of orbitals:

$$\Psi_{i_1 i_2 i_3 \cdots}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots) =$$

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_{i_1}(\vec{r}_1) & \phi_{i_1}(\vec{r}_1) & \phi_{i_1}(\vec{r}_1) & \cdots \\ \phi_{i_2}(\vec{r}_1) & \phi_{i_2}(\vec{r}_1) & \phi_{i_2}(\vec{r}_1) & \cdots \\ \phi_{i_3}(\vec{r}_1) & \phi_{i_3}(\vec{r}_1) & \phi_{i_3}(\vec{r}_1) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} \tag{16}$$

This relies on the properties of a determinant, which changes sign if you swap two rows or two columns. This means that if two of your orbitals are the same, the result will be zero, so the "occupancy" of any orbital is either 0 or 1. Note that the $N!$ is required in order to ensure that the wave function is normalized provided the orbitals are orthonormal.

1.3.2 Bosons

Bosons have integer spin, and differ from fermions in that their sign does not change when you interchange particles.

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots) = \Psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \cdots) \tag{17}$$

The wavefunction for noninteracting bosons looks very much like the Slater determinant above, only with a special version of the determinant that has all + signs. The bosons can have as many particles as they want in a given orbital. In the limiting case where all particles are in the same orbital, a single product of orbitals satisfies the required symmetry.

1.4 Fermi-Dirac distribution

Let us now consider a set of non-interacting fermions. These fermions have a Hamiltonian with a set of single-particle energy eigenvalues given by ε_i. How do we find the probability of any given many-body microstate? As always, the probability of any given microstate is given by the Boltzmann distribution, but given that are particles are non-interacting, we'd prefer to deal with just one at a time. As it turns out, dealing with one *particle* at a time is not really possible, but in a grand canonical ensemble we can deal with a single *orbital* at a time with much greater ease. We can think of each *orbital* as a separate system, and ask how many particles it has! Particles can now be exchanged between *orbitals* just like they were between systems last week.

Small groups Work out the grand partition function for a single orbital with energy ε_i that may occupied by a fermion.

Answer Now that we are thinking of an orbital as a system, we can pretty easily write down all the possible states of that system: it is either occupied or unoccupied. The latter case has 0 energy, and also $N = 0$, while the former case has energy ε and $N = 1$. Summing over these gives the

Gibbs sum

$$\mathcal{Z} = \sum_{i}^{\text{all } \mu\text{states}} e^{-\beta(\varepsilon_i - \mu N_i)} \tag{18}$$

$$= 1 + e^{-\beta(\varepsilon-\mu)} \tag{19}$$

Note that the same statistics would apply to a state for a classical particle if there were an infinite energy required to have two particles in the same state. The physics here is a system that can hold either zero or one particles, and there are various ways you could imagine that happening.

Small groups Find the energy and the average occupancy ($\langle N\rangle$) of the orbital

Answer If we want to find $\langle N\rangle$ of the system, we can do that in the usual way Finding is basically the same

$$\langle N\rangle = \sum_i N_i P_i \tag{20}$$

$$= \frac{0 + e^{-\beta(\varepsilon-\mu)}}{\mathcal{Z}} \tag{21}$$

$$= \frac{e^{-\beta(\varepsilon-\mu)}}{1 + e^{-\beta(\varepsilon-\mu)}} \tag{22}$$

$$= \frac{1}{1 + e^{\beta(\varepsilon-\mu)}} \tag{23}$$

Finding the energy is basically the same, since the energy is proportional to the occupancy:

$$\langle E\rangle = \sum_i E_i P_i \tag{24}$$

$$= \frac{0 + \varepsilon e^{-\beta(\varepsilon-\mu)}}{\mathcal{Z}} \tag{25}$$

$$= \varepsilon\langle N\rangle \tag{26}$$

The average occupancy of an orbital is called the Fermi-Dirac function, and is normally written as:

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon_i-\mu)} + 1} \tag{27}$$

Whenever you are looking at non-interacting fermions, $f(\varepsilon)$ will be very helpful.

Small groups Sketch the Fermi-Dirac function.

When talking about electrons, we often refer to the chemical potential μ as the **Fermi level**. Kittel also defines the **Fermi energy** ε_F as the Fermi *level* when the temperature is zero, i.e.

$$\varepsilon_F \equiv \mu(T = 0) \tag{28}$$

At zero temperature, all the orbitals with energy less than ε_F are occupied, while all the orbitals with higher energy are unoccupied.

Actual electrons You might (or might not) be wondering how we can talk about electrons as non-interacting particles. After all, they are charged particles, which naturally repel each other rather strongly. Indeed, a Slater determinant is a terrible approximation for an energy eigenstate for *any* many-electron system. So why are we bothering talking about orbitals and the Fermi-Dirac distribution that relies on orbitals being an actual thing?

I'm not going to thoroughly explain this, but rather just give a few hints about why what we're doing might be reasonable. The key idea is that what we are really interested in is the behavior of excited states of our many-body system. (The ground state is also very interesting, e.g. if you want to study vibrations or phonons, but not in terms of the thermal behavior of the electrons themselves.) Fortunately, even though the electrons really do interact with one another very strongly, it is possible to construct a picture of **elementary excitations** that treats these excitations as not interacting with one another. In this kind of a picture, what we are talking about are called **quasiparticles**. These represent an excitation of the many-body state. And it turns out that in many cases (particularly for solids) we can represent a given excited state of the many-body system as a sum of the energy of a bunch of non-interacting **quasiparticles**. When this breaks down, we invent new names like **exciton** to represent an excitation in which more than one quasiparticle are interacting.

1.5 Bose-Einstien distribution

The same ideas apply to bosons as to fermions: we can treat each orbital as a separate system in the grand canonical ensemble. In this case, however, the occupancy N can have any (non-negative) value.

Small groups Solve for the Gibbs sum for an orbital with energy ε, and solve for the $\langle N\rangle$ for a single orbital occupied by bosons.

Answer The Gibbs sum will be

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{-\beta(N\varepsilon-\mu N)} \tag{29}$$

$$= \sum_{n=0}^{\infty} \left(e^{-\beta(\varepsilon-\mu)}\right)^N \tag{30}$$

$$= \sum_{n=0}^{\infty} \left(e^{-\beta(\varepsilon-\mu)}\right)^N \tag{31}$$

This looks suspiciously like a simple harmonic oscillator. The same harmonic summation trick applies, and we see that

$$\mathcal{Z} = 1 + e^{-\beta(\varepsilon-\mu)} + \left(e^{-\beta(\varepsilon-\mu)}\right)^2 + \cdots \tag{32}$$

$$e^{-\beta(\varepsilon-\mu)}\mathcal{Z} = e^{-\beta(\varepsilon-\mu)} + \left(e^{-\beta(\varepsilon-\mu)}\right)^2 + \cdots \tag{33}$$

Subtracting the two gives

$$\left(1 - e^{-\beta(\varepsilon-\mu)}\right)\mathcal{Z} = 1 \tag{34}$$

$$\mathcal{Z} = \frac{1}{1 - e^{-\beta(\varepsilon-\mu)}} \tag{35}$$

Solving for the average occupancy $\langle N\rangle$ is again more tedious than for a fermion:

$$\begin{aligned}
\langle N\rangle &= \sum_i N_i P_i && (36)\\
&= \frac{1}{\mathcal{Z}}\sum_{N=0}^{\infty} N e^{-\beta(\varepsilon-\mu)N} && (37)\\
&= \frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\mu}\left(\frac{1}{\beta}\right) && (38)\\
&= -\frac{\cancel{1-e^{-\beta(\varepsilon-\mu)}}}{\left(1-e^{-\beta(\varepsilon-\mu)}\right)^{\cancel{2}}}\left(-e^{-\beta(\varepsilon-\mu)}\right)\cancel{\beta}\left(\frac{1}{\cancel{\beta}}\right) && (39)\\
&= \frac{e^{-\beta(\varepsilon-\mu)}}{1-e^{-\beta(\varepsilon-\mu)}} && (40)\\
f(\varepsilon) &= \frac{1}{e^{\beta(\varepsilon-\mu)}-1} && (41)
\end{aligned}$$

This turns out to be just the Planck distribution we aleady saw, only with a chemical potential as reference. Why does this bosonic system look like a simple harmonic oscillator? Since the particles are non-interacting, we have the same set of energy eigenvalues, which is to say an equally spaced series of states. This is conversely related to why we can describe solutions to the simple harmonic oscillator as bosonic phonons.

Small groups Sketch the Bose-Einstein distribution function.

This expression, the Bose-Einstein distribution, tells us that at low temperatures, we could end up seeing a *lot* of particles in low energy states (if there are any eigenvalues below μ), in contrast to the Fermi-Dirac distribution, which never sees more than one particle per state.

1.6 Entropy

Small groups Find the entropy of a single orbital that may hold a fermion.

Answer We begin with the probabilities of the two microstates:

$$P_0 = \frac{1}{\mathcal{Z}} \qquad\qquad P_1 = \frac{e^{-\beta(\varepsilon-\mu)}}{\mathcal{Z}} \tag{42}$$

where

$$\mathcal{Z} = 1 + e^{-\beta(\varepsilon-\mu)} \tag{43}$$

Now we just find the entropy using FINISH THIS!

1.7 Classical ideal gas

We are now prepared to talk about a gas in the **classical limit**. In the classical limit, there is no difference in behavior between fermions and bosons. This happens when the probability of finding a particle in a particular orbital is $\ll 1$. And *this* happens when $\beta(\varepsilon-\mu) \gg 1$ for all orbitals, i.e. when μ is very negative. When this is the case, both the Fermi-Dirac distribution and the Bose-Einstein distribution become identical.

$$f_{FD}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1} \approx e^{-\beta(\varepsilon-\mu)} \tag{44}$$

$$f_{BE}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}-1} \approx e^{-\beta(\varepsilon-\mu)} \tag{45}$$

In this limit (which is the low-density limit), the system will behave as a classical ideal gas.

A reasonable question is, "what is the chemical potential." We already handled this, but can now look at this answer in terms of orbitals and the classical distribution function. (Note: *classical distribution function* is a bit of a misnomer in this context, as it defines how many particles are in a given quantum mechanical orbital.)

$$\begin{aligned}
\langle N\rangle &= \sum_i^{\text{orbitals}} f(\varepsilon_i) &(46)\\
&= \sum_i^{\text{orbitals}} e^{-\beta(\varepsilon_i-\mu)} &(47)\\
&= e^{\beta\mu}\sum_i^{\text{orbitals}} e^{-\beta(\varepsilon_i)} &(48)\\
&= e^{\beta\mu} Z_1 &(49)\\
N &= e^{\beta\mu} n_Q V &(50)
\end{aligned}$$

where Z_1 is the partition function for a single particle in a box, which we derived a few weeks ago to be n_QV where $n_Q \equiv \left(\frac{mkT}{2\pi\hbar^2}\right)^{\frac{3}{2}}$. Thus we can once again find the expression we found last week, where

$$e^{\beta\mu} = \frac{1}{n_Q}\frac{N}{V} = \frac{n}{n_Q} \tag{51}$$

We can solve for the chemical potential

$$\mu = kT\left(\ln N - \ln V - \tfrac{3}{2}\ln(kT) + \tfrac{3}{2}\ln\left(2\pi\hbar^2/m\right)\right) \tag{52}$$

Thus it decreases as volume increases or as the temperature increases. We can further find the free energy by integrating the chemical potential. This is again redundant when compared with the approach we already solved for this. Remember that

$$dF = -SdT - pdV + \mu dN \tag{53}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} \tag{54}$$

Note that this must be an integral at fixed V and T:

$$\begin{aligned} F &= \int_0^N \mu dN \tag{55}\\ &= \int_0^N kT\left(\ln N - \ln V - \ln n_Q\right)dN \tag{56}\\ &= kT\left(N\ln N - N - N\ln V - N\ln n_Q\right) \tag{57}\\ &= NkT\left(\ln\left(\frac{n}{n_Q}\right) - 1\right) \tag{58}\end{aligned}$$

Small groups Solve for the entropy of the ideal gas (from this free energy).

Answer

$$\begin{aligned} -S &= \left(\frac{\partial F}{\partial T}\right)_{V,N} \tag{59}\\ &= Nk\left(\ln\left(\frac{n}{n_Q}\right) - 1\right) - \frac{NkT}{n_Q}\frac{dn_Q}{dT} \tag{60}\\ &= Nk\left(\ln\left(\frac{n}{n_Q}\right) - 1\right) - \frac{Nk\cancel{T}}{\cancel{n_Q}}\frac{3}{2}\cancel{\frac{n_Q}{T}} \tag{61}\\ -S &= Nk\left(\ln\left(\frac{n}{n_Q}\right) - \frac{5}{2}\right) \tag{62}\\ S &= Nk\left(\ln\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right) \tag{63}\end{aligned}$$

This expression for the entropy is known as the **Sackur-Tetrode** equation.

Small groups Solve for the pressure of the ideal gas (from the free energy)

Answer

$$\begin{aligned} p &= -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{64}\\ &= \frac{NkT}{V} \tag{65}\end{aligned}$$

That was pretty easy, once we saw that n_Q was independent of volume. This expression is known as the **ideal gas law**.

Small groups Solve for the internal energy of the ideal gas

Answer

$$\begin{aligned} U &= F + TS \tag{66}\\ &= \frac{3}{2}NkT \tag{67}\end{aligned}$$

Also pretty familiar.

Small groups Solve for the heat capacity at constant volume of the ideal gas

Answer

$$
\begin{aligned}
C_V &= \left(\frac{\partial U}{\partial T}\right)_{V,N} && (68)\\
&= T\left(\frac{\partial S}{\partial T}\right)_{V,N} && (69)\\
&= \frac{3}{2}Nk && (70)
\end{aligned}
$$

This one is relatively easy.

Small groups Solve for the heat capacity at constant pressure of the ideal gas

Answer

$$
\begin{aligned}
C_p &= T\left(\frac{\partial S}{\partial T}\right)_{p,N} && (71)\\
& && (72)
\end{aligned}
$$

This one requires one (small) step more. We have to convert the volume into a pressure in the free energy expression.

$$
\begin{aligned}
C_p &= T\left(\frac{\partial Nk\left(\ln\left(\frac{n_Q}{n}\right)+\frac{5}{2}\right)}{\partial T}\right)_{p,N} && (73)\\
&= NkT\left(\frac{\partial\left(\ln\left(\frac{n_Q}{n}\right)+\frac{5}{2}\right)}{\partial T}\right)_{p,N} && (74)\\
&= NkT\left(\frac{\partial \ln\left(\frac{Vn_Q}{N}\right)}{\partial T}\right)_{p,N} && (75)\\
&= NkT\left(\frac{\partial \ln\left(\frac{NkT}{p}\frac{n_Q}{N}\right)}{\partial T}\right)_{p,N} && (76)
\end{aligned}
$$

At this point we peek inside and see that $n_Q \propto T^{\frac{3}{2}}$ and can complete the derivative

$$
C_p = \frac{5}{2}Nk \qquad (77)
$$

This has been a series of practice computations involving the ideal gas. The results are useful for some of your homework, and the process of finding these properties is something you will need to know for the final exam. Ultimately, pretty much everything comes down to summing and integrating to find partition functions, and then taking derivatives (and occasional integrals) to find everything else.