Homework 5 Solutions

Problem 1 In our statistical mechanical analysis of the ideal gas (see the notes for lecture 7), we modelled the gas a system of point particles having three translational degrees of freedom. This is basically true for the monatomic gases such as helium and argon. However, diatomic gases such as nitrogen and argon, have two rotational degrees of freedom as well. The rigid rotator is a way of modelling this aspect just like the particle in a box is a way of modelling the translational degrees of freedom. The starting point is the Hamiltonian:

\[ E = \frac{L^2}{2I} \]

where \( L^2 \) takes on the values \( l(l+1)\hbar^2 \) and each \( l \) state is \( (2l+1) \)-fold degenerate. The partition function for a single rotator is then given by:

\[ Z = \sum_{l=0}^{\infty} g_l e^{-\frac{El}{\tau}} = \sum_{l=0}^{\infty} (2l + 1) e^{-\frac{l(l+1)\hbar^2}{2I\tau}} \]

(a) In the limit \( \tau >> \frac{\hbar^2}{2I} \), the spacing between successive energy levels is very small so we may approximate the sum as an integral (see page 7-3 of the lecture notes to see this same approximation done in the ideal gas context).

\[
Z \approx \int_{0}^{\infty} dx (2x + 1) e^{-\frac{x(x+1)\hbar^2}{2I\tau}} \\
= \int_{0}^{\infty} du e^{-\frac{u^2}{2\tau}} \\
= \frac{2I\tau}{\hbar^2} 
\]

From this, we can easily calculate other thermodynamic quantities:

\[
U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \tau^2 \cdot \frac{1}{\hbar^2} \cdot \frac{2I\tau}{\hbar^2} = \tau \\
F = -\tau \log Z = -\tau \log( \frac{2I\tau}{\hbar^2} ) \\
\sigma = \frac{U - F}{\tau} = \frac{\tau + \tau \log( \frac{2I\tau}{\hbar^2} )}{\tau} = 1 + \log( \frac{2I\tau}{\hbar^2} )
\]

Notice that \( U = \tau \), which is consistent with the classical equipartition theorem, which states that each degree of freedom contributes \( \frac{1}{2} \tau \) to the internal energy. A rigid rotator has two degrees of freedom so \( U = \tau \). Another point is that at high temperatures, the entropy of a rotator becomes very large, which roughly means that there are a large number of states in which the rotator can effectively be in. Of course, there are an infinite number of possible states but the probabilities
of most of them are so small that they are not states in which the rotator can “effectively” be in (i.e. like the theoretically possibly state of a gas in a room where all the gas is in one half of the room — see Homework 1, problem 2).

(b) When $\tau << \frac{\hbar^2}{2I}$, the probabilities of all but the first few levels is negligible. Therefore, we may approximate the partition function by the first few terms:

$$Z \approx 1 + 3e^{\frac{-\hbar^2}{2I\tau}} + \cdots$$

The other thermodynamic quantities are found in the usual way:

$$U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \tau^2 \cdot \frac{1}{1 + 3e^{\frac{-\hbar^2}{2I\tau}}} \cdot 3e^{\frac{-\hbar^2}{2I\tau}} \cdot \left(\frac{\hbar^2}{2I\tau}\right) = \frac{3e^{\frac{-\hbar^2}{2I\tau}}}{1 + 3e^{\frac{-\hbar^2}{2I\tau}}} \left(\frac{\hbar^2}{I\tau}\right)\tau$$

$$F = -\tau \log Z = -\tau \log(1 + 3e^{\frac{-\hbar^2}{2I\tau}})$$

$$\sigma = \frac{U - F}{\tau} = \frac{3e^{\frac{-\hbar^2}{2I\tau}}}{1 + 3e^{\frac{-\hbar^2}{2I\tau}}} \left(\frac{\hbar^2}{I\tau}\right) + \log(1 + 3e^{\frac{-\hbar^2}{2I\tau}})$$

Notice that the entropy becomes very small at very low temperatures. This means that effectively, there are relatively few states in which the rotator can exist. Also notice that the rotational energy vanishes at low temperatures so that at such temperatures, all the energy is in the translational modes. In other words, if a diatomic gas is cooled to sufficiently low temperatures (and assuming it remains a gas), its effective heat capacity would be given by $c_v = \frac{5}{2}k_B$, instead of $\frac{3}{2}k_B$, which is the high temperature result.

(c) The last part of the problem asks what temperature constitutes a “low” temperature. The dividing temperature is given by $\tau = \frac{\hbar^2}{2I}$. For nitrogen, we can take $R \sim 10^{-10}m$, $M \sim 28 \times m_{\text{proton}}$, $I \sim MR^2$, and:

$$\Theta_R(\text{in K}) = \frac{\hbar^2}{2Ik_B} = \frac{(1.05 \times 10^{-34})^2}{2(28 \times 1.67 \times 10^{27})(10^{-10})^2(1.38 \times 10^{-23})} \approx 0.085K$$

This tells us that at room temperature, a diatomic gas will have its rotational modes excited. In other words, its heat capacity will be $c_v = \frac{5}{2}k_B$.

Problem 2 Kittel 6-1 The Fermi-Dirac distribution function, which gives the thermal average number of particles in an energy level with energy $\epsilon$, is given by:

$$f(\epsilon) = \frac{1}{\exp(\frac{\epsilon - \mu}{\tau}) + 1}$$

Differentiating:

$$-\left(\frac{\partial f}{\partial \epsilon}\right)_{\epsilon=\mu} = \left(\frac{\frac{1}{\tau} \exp(\frac{\epsilon - \mu}{\tau})}{(\exp(\frac{\epsilon - \mu}{\tau}) + 1)^2}\right)_{\epsilon=\mu} = \frac{1}{4\tau}$$
So the Fermi-Dirac function gets steeper about the Fermi energy at low temperatures.

**Problem 3 Kittel 6-3**

![Possible states of the system discussed in part (a) and part (b).](image)

**(a)** In drawing (a) of the figure, we have the three possible states (and corresponding energies) of our system, which is a single orbital that can hold 0, 1, or 2 particles. The partition function for this system is:

\[
Z = \sum_{SN} \lambda^N e^{-E_s/\tau} = \lambda^0 e^0 + \lambda^1 e^{-E/\tau} + \lambda^2 e^{-2E/\tau} = 1 + \lambda e^{-E/\tau} + \lambda^2 e^{-2E/\tau}
\]

And the average particle number:

\[
<N> = \frac{1}{Z} \sum_{SN} N\lambda^N e^{-E_s/\tau} = \frac{\lambda e^{-E/\tau} + 2\lambda^2 e^{-2E/\tau}}{1 + \lambda e^{-E/\tau} + \lambda^2 e^{-2E/\tau}}
\]

**(b)** In drawing (b) of the figure, we have the four possible states (and energies) corresponding to our system, which is a pair of degenerate orbitals, each of which may hold 0 or 1 particle. The partition function is:

\[
Z = \sum_{SN} \lambda^N e^{-E_s/\tau} = 1 + \lambda e^{-E/\tau} + \lambda e^{-E/\tau} + \lambda^2 e^{-2E/\tau} = 1 + 2\lambda e^{-E/\tau} + \lambda^2 e^{-2E/\tau}
\]

And the average particle number:

\[
<N> = \frac{1}{Z} \sum_{SN} N\lambda^N e^{-E_s/\tau} = \frac{2\lambda e^{-E/\tau} + 2\lambda^2 e^{-2E/\tau}}{1 + 2\lambda e^{-E/\tau} + \lambda^2 e^{-2E/\tau}}
\]

**Problem 4 Kittel 6-4** One way to do this problem is to remind ourselves of how the usual classical result is obtained. The energy of a single free particle is given by:

\[
E = \frac{p^2}{2m}
\]
The partition function is a sum over states, where in this case a “state” refers to a particular momentum:

\[
Z = \int d^3p e^{-\frac{p^2}{2m\tau}} = \left(\frac{2\pi m\tau}{\hbar}\right)^{\frac{3}{2}}
\]

\[
U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \tau^2 \cdot \frac{(2\pi m)^{3/2}}{(2\pi m\tau)^{3/2}} \cdot \frac{3}{2} \tau = \frac{3}{2} \tau
\]

For the relativistic case, it is exactly the same except our dispersion relation is now:

\[
E = pc
\]

\[
Z = \int d^3p e^{-\frac{pc}{\hbar c}} = \int d\phi d\theta \sin \theta p^2 d\rho e^{-\frac{pc}{\hbar c}} = \frac{8\pi \tau^3}{c^3}
\]

\[
U = \tau^2 \frac{\partial \log Z}{\partial \tau} = \tau^2 \cdot \frac{24\pi \tau^2}{8\pi \tau} = 3 \tau
\]

**Problem 5 Kittel 6-9** We will consider a single orbital \(\epsilon_n\) corresponding to the quantum number \(n = (n_x, n_y, n_z)\) of the center of mass Hamiltonian. If the atom has internal degrees of freedom, then as stated on page 169 of Kittel, the grand partition function is:

\[
Z_n = 1 + \lambda Z_{\text{int}} e^{-\epsilon_n/\tau} = 1 + \lambda \left(e^{-\epsilon/\tau} + e^{-(\epsilon+\Delta)/\tau}\right) \exp(-\epsilon_n/\tau)
\]

where \(\epsilon\) and \(\epsilon + \Delta\) are the two internal energy levels. The full partition function is a product of the single level functions:

\[
Z = \prod_n \left(1 + \lambda Z_{\text{int}} e^{-\epsilon_n/\tau}\right)
\]

We may obtain the chemical potential by first calculating the average particle number:

\[
<N> = \lambda \frac{\partial (\log Z)}{\partial \lambda} = \lambda \frac{\partial}{\partial \lambda} \left(\sum_n \log(1 + \lambda Z_{\text{int}} e^{-\epsilon_n/\tau})\right)
\]

\[
= \sum_n \frac{\lambda Z_{\text{int}} e^{-\epsilon_n/\tau}}{1 + \lambda Z_{\text{int}} e^{-\epsilon_n/\tau}}
\]
Because we are considering an ideal gas, we are assuming the occupancy is low (see the discussion on page 14-4). In this case, we may make the approximation:

\[ < N > \approx \lambda Z_{\text{int}} \sum_n e^{-\epsilon_n/\tau} = \lambda Z_{\text{int}} Z_1 = \lambda Z_{\text{int}} nQV \]

Therefore,

\[ \lambda = \frac{n}{nQZ_{\text{int}}} \]

which implies that

\[ \mu = \tau \log \frac{n}{nQZ_{\text{int}}} \]

To obtain the free energy, we note that:

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

\[ \Rightarrow F = \int \left( \frac{\partial F}{\partial N} \right)_{\tau,V} dN = N \tau \left( \log \frac{n}{nQZ_{\text{int}}} - 1 \right) = N \tau (\log \frac{n}{nQ} - 1) - N \tau \log Z_{\text{int}} \]

The entropy is obtained using by differentiating the free energy (where we recognize that part of the free energy merely gives the usual ideal gas result):

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

\[ = N \left( \log \frac{nQ}{n} + \frac{5}{2} \right) + N \left( \frac{\partial (\tau \log Z_{\text{int}})}{\partial \tau} \right)_V \]

\[ = N \left( \log \frac{nQZ_{\text{int}}}{n} + \frac{5}{2} \right) + N \tau \left( \frac{\partial (\log Z_{\text{int}})}{\partial \tau} \right)_V \]

\[ = N \left( \log \frac{nQZ_{\text{int}}}{n} + \frac{5}{2} \right) + N \tau \left( \frac{e^{-\epsilon/\tau} + e^{-\epsilon+\Delta)/\tau}}{e^{-\epsilon/\tau} + e^{-\epsilon+\Delta)/\tau}} \right) \]

\[ = N \left( \log \frac{nQZ_{\text{int}}}{n} + \frac{5}{2} \right) + N \left( \frac{\epsilon}{\tau} + \frac{e^{-\epsilon+\Delta)/\tau}}{e^{-\epsilon/\tau} + e^{-\epsilon+\Delta)/\tau}} \right) \]

\[ = N \left( \log \frac{nQZ_{\text{int}}}{n} + \frac{5}{2} \right) + N \left( \frac{\epsilon}{\tau} + \frac{\Delta/\tau}{e^{\Delta/\tau} + 1} \right) \]

\[ = N \left( \log \frac{nQZ_{\text{int}}}{n} + \frac{5}{2} + \frac{\epsilon}{\tau} + \frac{\Delta/\tau}{e^{\Delta/\tau} + 1} \right) \]

The pressure is straightforward. Because the internal partition function does not depend on volume, the result is the same as the usual ideal gas:

\[ p = - \left( \frac{\partial F}{\partial V} \right)_{\tau,N} = \frac{N}{V} \tau + \frac{\partial}{\partial V} \left( N \tau \log Z_{\text{int}} \right)_{\tau,N} = \frac{N}{V} \tau \]
The heat capacity at constant pressure is obtained by differentiating the entropy. Once again, we recognize terms as producing the usual ideal gas result as well as some additional terms:
\[
c_p = \tau \left( \frac{\partial \sigma}{\partial \tau} \right)_p = N \tau \frac{\partial}{\partial \tau} \left( \log \frac{nQ}{n} + \frac{5}{2} \right)_p + N \tau \frac{\partial}{\partial \tau} \left( \log Z_{\text{int}} + \frac{\epsilon}{\tau} + \frac{\Delta/\tau}{e^\Delta/\tau + 1} \right)_p
\]
\[
= N \left( \frac{5}{2} + \frac{e^{\Delta/\tau}}{(e^{\Delta/\tau} + 1)^2} \left( \frac{\Delta}{\tau} \right)^2 \right)
\]

**Problem 6 Kittel 6-10 (a)** These relations follow by logarithmically differentiating the isentropic expansion formulae on page 174 of Kittel:

\[
pV^\gamma = k_1 \Rightarrow dp \frac{p}{p} + \gamma dV \frac{V}{V} = 0
\]
\[
\tau V^{\gamma-1} = k_2 \Rightarrow d\tau \frac{\tau}{\tau} + (\gamma - 1) dV \frac{V}{V} = 0
\]
\[
\rho v \tau^{\gamma-1} = k_3 \Rightarrow dp \frac{p}{p} + \frac{\gamma}{1 - \gamma} d\tau \frac{\tau}{\tau} = 0
\]
where \(k_1, k_2,\) and \(k_3\) are constants.

(b) At constant entropy, we have the following relation for an ideal gas:
\[
dU = -pdV = c_v d\tau \Rightarrow d\tau \frac{dV}{dV} = \frac{-p}{c_v}
\]
Then:
\[
B_\sigma = -V \left( \frac{\partial p}{\partial V} \right)_\sigma = -V \frac{\partial}{\partial V} \left( \frac{N \tau}{V} \right)_\sigma
\]
\[
= -V \left( -\frac{N \tau}{V^2} + \frac{N}{V} \left( \frac{\partial \tau}{\partial V} \right)_\sigma \right)
\]
\[
= \frac{N \tau}{V} + \frac{Np}{c_v}
\]
\[
= \frac{p \cdot c_v + N}{c_v}
\]
\[
= \gamma p
\]

And:
\[
B_\tau = -V \left( \frac{\partial p}{\partial V} \right)_\tau = -V \frac{\partial}{\partial V} \left( \frac{N \tau}{V} \right)_\tau = V \cdot \frac{N \tau}{V^2} = \frac{N \tau}{V} = p
\]

**Problem 7 Kittel 6-11 (a)** The figure shows the situation. Mechanical equilibrium requires that the pressures acting on the surfaces of this slice balance the weight of the slice.
\[
p(z + dz) + \rho(z)gdz = p(z) \Rightarrow \frac{dp}{dz} = -\rho g
\]
The entropy is constant in the $z$ direction so we can relate the derivatives of $P$ and $T$ using the isentropic relation found in the previous problem:

$$\frac{dp}{dz} = \frac{\gamma - 1}{\gamma} \frac{d\tau}{dz}$$

And the ideal gas law links $\rho(z)$ to $p(z)$ and $\tau(z)$:

$$p = \frac{N\tau}{V} = \frac{M\tau}{M_{N_2}V} = \frac{\rho\tau}{M_{N_2}}$$

Putting these relations together:

$$\frac{d\tau}{dz} = \frac{\gamma - 1}{\gamma} \frac{dp}{dz}$$

$$= -\frac{\gamma - 1}{\gamma} \frac{\rho g}{p}$$

$$= -\frac{\gamma - 1}{\gamma} \frac{M_{N_2}g \rho}{p}$$

$$\frac{dT}{dz} = -\frac{\gamma - 1}{\gamma} \frac{M_{N_2}g}{k_B}$$

(b)

$$\frac{dT}{dz} \approx -0.428 \times 1.67 \times 10^{-27} \times 9.8 \approx -10^{-7} \frac{K}{m} = -10 \frac{K}{km}$$

(c) $p \sim V^{-\gamma} \sim (1/\rho)^{-\gamma} = \rho^\gamma$.

**Problem 8 Kittel 6-15** The gas is isentropically compressed by a ratio of 15 which implies:

$$T_f = T_i \left( \frac{V_i}{V_f} \right)^{\gamma - 1} = 300(K)(15)^{0.4} = 886K$$