K&K 2.1
Part a
Suppose $g(U) = CU^{3N/2}$, where C is a constant and N is the number of particles. Show that $U = \frac{3}{2}N\tau$.
We use the definition of temperature as

$$\frac{\partial \sigma}{\partial U}\bigg|_N = \frac{1}{\tau} \tag{1}$$

So, let's calculate σ.

$$\sigma = ln(g) = \frac{3N}{2}ln(U) + ln(C) \tag{2}$$

Therefore,

$$\frac{\partial \sigma}{\partial U} = \frac{3N}{2U} = \frac{1}{\tau} \tag{3}$$

So finally,

$$U = \frac{3}{2}N\tau \quad \square \tag{4}$$

Part b
Show that $\partial^2\sigma/\partial U^2|_N$ is negative. This form of $g(U)$ actually applies to an ideal gas.
Referring to the definition of $\frac{\partial \sigma}{\partial U}$ in equation 3 and taking another derivative:

$$\frac{\partial^2 \sigma}{\partial U^2} = -\frac{3N}{2U^2} < 0 \quad \square \tag{5}$$

This suggests that the temperature of the system will increase with increasing U.

K&K 2.2
Find the equilibrium value at temperature τ of the fractional magnetization $M/Nm = 2\langle s\rangle/N$ of the system of N spins each of magnetic moment m in a magnetic field B. The spin excess is 2s. Take the entropy as the logarithm of the multiplicity as given in 1.35: $\sigma(s) \approx log\{g(N,0)\} - 2s^2/N$.
The energy of a single magnetic moment **m** in a magnetic field **B** is $U = -\mathbf{m} \cdot \mathbf{B}$. A spin excess of 2s means that there are 2s spins with this magnetic moment. In other words, there could be, say, 3s particles of magnetic moment **m** and 1s particles of magnetic moment $-\mathbf{m}$. The energy would cancel for all but 2s particles. Thus, the total energy of the system is $U = -2smB$. Therefore, $s = -U/2mB$. So the entropy is

$$\sigma = \sigma_0 - \frac{2s^2}{N} = \sigma_0 - \frac{U^2}{2m^2B^2N} \tag{6}$$

Since $1/\tau = \partial\sigma/\partial U$, we find

$$\frac{\partial \sigma}{\partial U} = -\frac{U}{m^2B^2N} = \frac{1}{\tau} \quad \Rightarrow \quad U = -\frac{m^2B^2N}{\tau} \tag{7}$$

Finally, we know that $U = -MB$ since the energy is the total magnetization times the magnetic field. Therefore,

$$-\frac{m^2B^2N}{\tau} = -MB \quad \Rightarrow \quad \frac{M}{Nm} = \frac{mB}{\tau} \quad \square \tag{8}$$

Note that the magnetic susceptibility obeys Curie's law $\chi \sim M/B \sim 1/\tau$.

K&K 2.3
Part a
Find the entropy of a set of N oscillators of frequency ω as a function of the total

quantum number n. Use the multiplicity function 1.55 and make the Stirling approximation. Replace $N - 1$ by N.

The general expression for the possible ways to obtain the energy $n\hbar\omega$ amongst a system of N harmonic oscillators is (equation 1.55):

$$g(N, n) = \frac{(N + n - 1)!}{n!(N - 1)!} \tag{9}$$

Making the approximation that N is large, we get:

$$g(N, n) = \frac{(N + n)!}{n!N!} \tag{10}$$

from which the entropy $\sigma = ln(g)$ is:

$$\sigma = ln(g) = ln\{(N + n)!\} - ln(n!) - ln(N!) \tag{11}$$

Invoking Stirling's approximation:

$$\sigma \approx (N + n)ln(N + n) - Nln(N) - nln(n) \quad \Box \tag{12}$$

where I have canceled out some terms.

Part b

Let U denote the total energy $n\hbar\omega$ of the oscillators. Express the entropy as $\sigma(U, N)$. Show that the total energy at temperature τ is

$$U = \frac{N\hbar\omega}{exp(\hbar\omega/\tau) - 1}. \tag{13}$$

This is the Planck result for the energy of a system of N harmonic oscillators.

The total energy of the system is $U = n\hbar\omega$. Thus, we replace n in expression 12 with $U/\hbar\omega$:

$$\sigma = (N + \frac{U}{\hbar\omega})ln(N + \frac{U}{\hbar\omega}) - Nln(N) - \frac{U}{\hbar\omega}ln(\frac{U}{\hbar\omega}) \tag{14}$$

Now we can do a little rearranging:

$$\sigma = Nln(\frac{N + \frac{U}{\hbar\omega}}{N}) + \frac{U}{\hbar\omega}ln(\frac{N + \frac{U}{\hbar\omega}}{\frac{U}{\hbar\omega}}) = Nln(1 + \frac{U}{N\hbar\omega}) + \frac{U}{\hbar\omega}ln(1 + \frac{N\hbar\omega}{U}) \tag{15}$$

Next, we use the thermodynamic definition of temperature $\partial\sigma/\partial U = 1/\tau$, to calculate $1/\tau$:

$$\frac{\partial\sigma}{\partial U} = \frac{N}{1 + \frac{U}{N\hbar\omega}}\frac{1}{N\hbar\omega} + \frac{1}{\hbar\omega}ln(1 + \frac{N\hbar\omega}{U}) - \frac{U}{\hbar\omega}\frac{N\hbar\omega}{U^2}\frac{1}{1 + \frac{N\hbar\omega}{U}} = \frac{1}{\tau} \tag{16}$$

Cleaning up the expression a bit, we see that the first and last terms in the derivative actually cancel:

$$\frac{\partial\sigma}{\partial U} = \frac{N}{N\hbar\omega + U} + \frac{1}{\hbar\omega}ln(1 + \frac{N\hbar\omega}{U}) - \frac{N}{U + N\hbar\omega} = \frac{1}{\hbar\omega}ln(1 + \frac{N\hbar\omega}{U}) = \frac{1}{\tau} \tag{17}$$

which we can easily solve for U:

$$1 + \frac{N\hbar\omega}{U} = exp(\frac{\hbar\omega}{\tau}) \quad \Rightarrow \quad U = \frac{N\hbar\omega}{exp(\frac{\hbar\omega}{\tau}) - 1} \quad \Box \tag{18}$$

K&K 2.4
Suppose that 10^{10} monkeys have been seated at typewriters throughout that age of the Universe, 10^{18} seconds. This number of monkeys is about three times greater than the

present human population of the earth. We suppose that a monkey can hit 10 type-writer keys per second. A typewriter may have 44 keys; we accept lowercase letters in place of capital letters. Assuming that Shakespeare's *Hamlet* has 10^5 characters, will the monkeys hit upon *Hamlet*?

Part a: Show that the probability that any given sequence of 10^5 characters typed at random will come out in the correct sequence is of the order of $44^{-100000} = 10^{-164345}$.

There are 44 keys on a typewriter, so the probability that the first letter is correct is $1/44$. The probability that the second letter is correct is $1/44$, etc. Since we need *all* the letters to be correct, we need to raise $1/44$ to the power of the number of letters in *Hamlet*:

$$\frac{1}{44}^{100000} = 44^{-100000} = 10^{-log_{10}(44) \times 100000} = 10^{-164345} \quad \square \tag{19}$$

where I have used the fact that $log_{10}(4) = 1.64345$.

Part b: Show that the probability that a monkey-*Hamlet* will be typed in the age of the Universe is approximately $10^{-164316}$.

Since a monkey types 10 letters a second, and the age of the Universe is 10^{18} seconds, the total number of letters that can be typed by one monkey in that time is 10^{19}. The monkey is able to start with any of them except for the last $10^{19} - (10^5 - 1) \approx 10^{19}$ of them. Now, the probability that a sequence of 10^5 letters will yield *Hamlet* is given in equation 19. Since there are $\approx 10^{19}$ characters that it can start typing with in order to create *Hamlet*, the probability that one monkey will type *Hamlet* in the age of the Universe is

$$P(Hamlet, 1 Monkey) = 10^{19} 10^{-164345} \tag{20}$$

so the probability that 10^{10} monkeys will do it is (just multiplying by 10^{10}):

$$P(Hamlet) = 10^{10} 10^{19} 10^{-164345} = 10^{-164316} \quad \square \tag{21}$$

K&K 2.5

Given two systems of $N_1 = N_2 = 10^{22}$ spins with multiplicity functions $g_1(N_1, s_1)$ and $g_2(N_2, s - s_1)$, the product $g_1 g_2$ as a function of s_1 is relatively sharply peaked at $s_1 = \hat{s}_1$. For $s_1 = \hat{s}_1 + 10^{12}$, the product $g_1 g_2$ is reduced by 10^{-174} from its peak value. Use the Gaussian approximation the multiplicity function.

Part a

Compute $g_1 g_2 / (g_1 g_2)_{max}$ for $s_1 = \hat{s}_1 + 10^{11}$ and $s = 0$.

We use equation 17 in K&K, which describes the number of states in a configuration of deviation δ from equilibrium:

$$g_1(N_1, \hat{s}_1 + \delta) g_2(N_2, \hat{s}_2 - \delta) = (g_1 g_2)_{max} exp(-\frac{2\delta^2}{N_1} - \frac{2\delta^2}{N_2}) \tag{22}$$

with $\delta = 10^{11}$ and $N = 10^{22}$, we get

$$\frac{g_1 g_2}{(g_1 g_2)_{max}} = exp(-\frac{2 \times (10^{11})^2}{10^{22}} - \frac{2 \times (10^{11})^2}{10^{22}}) \approx 0.0183 \quad \square \tag{23}$$

If the deviation δ is even an order of magnitude different, the multiplicity is incredibly different. 0.0183 corresponds to a deviation of 10^{11} from equilibrium, while for a deviation of 10^{12} the result would be 10^{-174}. Plotting equation 22 on a log-log plot with $N_1 = N_2 = 10^{22}$ reveals basically a line that drops almost precisely at $\delta = 10^{11}$.

K&K 3.1

Part a

Find an expression for the free energy as a function of τ of a system with two states, one at energy 0 and one at energy ϵ.

The partition function is:

$$Z = exp(-0/\tau) + exp(-\epsilon/\tau) = 1 + exp(-\epsilon/\tau) \tag{24}$$

and the free energy is related to the partition function by $F = -\tau ln(Z)$, so:

$$F = -\tau ln(Z) = -\tau ln(1 + exp(-\epsilon/\tau)) \quad \square \tag{25}$$

Part b
From the free energy, find expressions for the energy and entropy of the system.
The energy is calculated from the derivative of the partition function, but I am just going to write the normalized energy explicitly:

$$U = \frac{0 \times exp(-0/\tau) + \epsilon \times exp(-\epsilon/\tau)}{exp(-0/\tau) + exp(-\epsilon/\tau)} = \epsilon \frac{exp(-\epsilon/\tau)}{1 + exp(-\epsilon/\tau)} \quad \square \tag{26}$$

and the entropy can be calculated by $\sigma = -\partial F/\partial \tau$ at constant volume:

$$\sigma = \frac{\partial}{\partial \tau} \tau ln(1 + exp(-\epsilon/\tau)) = ln(1 + exp(-\epsilon/\tau)) + \frac{exp(-\epsilon/\tau)}{1 + exp(-\epsilon/\tau)} \left(\frac{\epsilon}{\tau}\right) \quad \square \tag{27}$$

As a sanity check, note that $U - \tau\sigma$ reproduces F. Furthermore, note that $\sigma \to 0$ as $\tau \to 0$, consistent with the third law of thermodynamics. As $\tau \to \infty, \sigma \to ln(2)$.

K&K 3.2
Part a
Use the partition function to find an exact expression for the magnetization M and the susceptibility $\chi = dM/dB$ as a function of temperature and magnetic field for the model system of magnetic moments in a magnetic field. The result for the magnetization is $M = nmtanh(mB/\tau)$, where n is the particle concentration.
The energy of a single magnetic moment is $\epsilon = \pm \mathbf{m} \cdot \mathbf{B}$, depending on the orientation of the moment. Therefore the partition function is:

$$Z = exp(-mB/\tau) + exp(mB/\tau) = 2cosh(mB/\tau) \tag{28}$$

and the average magnetic moment at temperature τ is

$$\langle m \rangle = \frac{m \times exp(-mB/\tau) - m \times exp(mB/\tau)}{exp(-mB/\tau) + exp(mB/\tau)} = mtanh(mB/\tau) \tag{29}$$

So to find the total magnetization, we need to multiply by the particle concentration n:

$$M = mntanh(mB/\tau) \quad \square \tag{30}$$

Thereofre, the susceptibility is

$$\chi = \frac{dM}{dB} = \frac{nm^2}{\tau} sech^2(mB/\tau) \quad \square \tag{31}$$

Part b
Find the free energy and express the result as a function only of τ and the parameter $x \equiv M/nm$.
The free energy is
$$F = -\tau ln(Z) = -\tau ln(2cosh(mB/\tau)) \tag{32}$$

To get this in the desired form, we used the trig identity $sech^2 x = 1 - tanh^2 x$, so $coshx = \sqrt{1/1 - tanh^2 x}$. Therefore, the free energy can be written as:

$$F = -\tau ln(2\sqrt{\frac{1}{1 - tanh^2(mB/\tau)}}) = -\frac{\tau}{2}ln(\frac{4}{1 - (\frac{M}{nm})^2}) = \frac{\tau}{2}ln(\frac{1 - x^2}{4}) \quad \square \tag{33}$$

Part c
Show that the susceptibility is $\chi = nm^2/\tau$ in the limit $mB \ll \tau$.

This follows directly from equation 31 and the fact that $sech^2x \to 1$ for $x \ll 1$. □

K&K 3.3

Part a

A one dimensional harmonic oscillator has an infinite series of equally spaced energy states, with $\epsilon_s = s\hbar\omega$, where s is a positive integer or zero, and ω is the classical frequency of the oscillator. We have chased the zero of energy at the state $s = 0$. Show that for a harmonic oscillator, the free energy is

$$F = \tau ln(1 - exp(-\hbar\omega/\tau)) \tag{34}$$

Note that at high temperatures such that $\tau \gg \hbar\omega$ we may expand the argument of the logarithm to obtain $F \approx ln(\hbar\omega/\tau)$.

The partition function for this system is:

$$Z = \sum_{s=0}^{\infty} exp(-s\hbar\omega/\tau) = \frac{1}{1 - exp(-\frac{\hbar\omega}{\tau})} \tag{35}$$

The free energy is related to the partition function by $F = -\tau ln(Z)$, so:

$$F = -\tau ln\{\frac{1}{1 - exp(-\frac{\hbar\omega}{\tau})}\} = \tau ln\{1 - exp(-\hbar\omega/\tau)\} \quad \square \tag{36}$$

Part b

From equation 34 show that the entropy is

$$\sigma = \frac{\hbar\omega/\tau}{exp(\hbar\omega/\tau) - 1} - ln(1 - exp(-\hbar\omega/\tau)) \tag{37}$$

The entropy is related to the free energy by $\sigma = -\partial F/\partial\tau$. Thus:

$$\sigma = -\frac{\partial}{\partial\tau}\tau ln\{1 - exp(-\hbar\omega/\tau)\} = -ln\{1 - exp(-\hbar\omega/\tau)\} + \frac{\hbar\omega/\tau}{exp(\hbar\omega/\tau) - 1} \quad \square \tag{38}$$

K&K 3.4

Consider a system of fixed volume in thermal contact with a reservoir. Show that the mean square fluctuation in the energy of the system is

$$\langle(\epsilon - \langle\epsilon\rangle)^2\rangle = \tau^2 \frac{\partial U}{\partial\tau}\Big|_V \tag{39}$$

Here U is the conventional symbol for $\langle\epsilon\rangle$. Hint: Use the partition function Z to relate $\partial U/\partial\tau$ to the mean square fluctuation. Also, multiply out the term $(...)^2$. Note: The temperature τ of a system is a quantity that by definition does not fluctuate in value when the system is in thermal contact with a reservoir. Any other attitude would be inconsistent with our definition of the temperature of a system. The energy of such a system may fluctuate, but the temperature does not. Some workers do not adhere to a rigorous definition of temperature. Thus Landau and Lifshitz give the result $\langle(\Delta\tau)^2\rangle = \tau^2/C_V$, but this should be viewed as just another form of equation 39, with $\Delta\tau$ set equal to $\Delta U/C_V$. We know that $\Delta U = C_V\Delta\tau$, whence the Landau-Lifshitz result becomes $\langle(\Delta U)^2\rangle = \tau^2 C_V$ which is our result (equation 39).

We first use the fact that

$$\langle(\epsilon - \langle\epsilon\rangle)^2\rangle = \langle\epsilon^2\rangle - \langle\epsilon\rangle^2 \tag{40}$$

Next, we recall the definition of the average energy: $U \equiv \langle\epsilon\rangle = (-1/Z)\partial Z/\partial\beta|_V$. where $\beta = 1/\tau$. Similarly, $\langle\epsilon^2\rangle = (1/Z)\partial^2 Z/\partial\beta^2|_V$. Therefore:

$$\langle\epsilon^2\rangle - \langle\epsilon\rangle^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}(\frac{\partial Z}{\partial\beta})^2 = \frac{\partial}{\partial\beta}(\frac{1}{Z}\frac{\partial Z}{\partial\beta}) = -\frac{\partial U}{\partial\beta} \tag{41}$$

where everything is understood to be at constant volume. Since $\beta = 1/\tau$, $d\beta = -d\tau/\tau^2$, meaning that:

$$\langle\epsilon^2\rangle - \langle\epsilon\rangle^2 = -\frac{\partial U}{\partial \beta}\Big|_V = \tau^2 \frac{\partial U}{\partial \tau}\Big|_V \quad \square \tag{42}$$

K&K 3.5
Overhauser Effect. **Suppose that by a suitable external mechanical or electrical arrangement one can add $\alpha\epsilon$ to the energy of the heat reservoir whenever the reservoir passes to the system the quantum of energy ϵ. The net increase of energy of the reservoir is $(\alpha - 1)\epsilon$. Here α is some numerical factor, positive or negative. Show that the effective Boltzmann factor for this abnormal system is given by**

$$P(\epsilon) \propto exp(-(1 - \alpha)\epsilon/\tau). \tag{43}$$

This reasoning gives the statistical basis of the Overhauser effect whereby the nuclear polarization in a magnetic field can be enhanced above the thermal equilibrium polarization. Such a condition requires the active supply of energy to the system from an external source. The system is not in equilibrium, but said to be in a steady state.
Let U_0 be the energy of the reservoir when the system has 0 energy. Then, when the reservoir gives energy ϵ to the system, it gains energy $\alpha\epsilon$, so that its energy after this transfer is $U_0 - \epsilon + \alpha\epsilon = U_0 - (1-\alpha)\epsilon$. Now, the probability to find the system in a state with energy ϵ_{sys} is proportional to the number of states of the system with that energy, and therefore is also proportional to the number of states of the reservoir with energy $U_0 - (1-\alpha)\epsilon_{sys}$, i.e. $P(\epsilon_{sys}) \propto g_R(U_0 - (1-\alpha)\epsilon_{sys})$. Following the book, we can write:

$$P(\epsilon) \propto g_R(U_0 - (1-\alpha)\epsilon_{sys}) = exp\{ln[g_R(U_0 - (1-\alpha)\epsilon_{sys})]\} = exp\{\sigma_R(U_0 - (1-\alpha)\epsilon_{sys})\} \tag{44}$$

where I have used the definition of entropy $\sigma = ln(g)$. Now if we expand the entropy in a Taylor series, we have:

$$\sigma_R(U_0 - (1-\alpha)\epsilon_{sys})\} = \sigma_R(U_0) - (1-\alpha)\epsilon_{sys}\frac{\partial\sigma}{\partial U} = \sigma_R(U_0) - (1-\alpha)\epsilon_{sys}/\tau \tag{45}$$

where I have used the thermodynamic definition of temperature in the last equality. Inserting this into equation 44, we get:

$$P(\epsilon) = exp(\sigma_R(U_0) - (1-\alpha)\epsilon_{sys}/\tau) \propto exp(-(1-\alpha)\epsilon_{sys}/\tau) \quad \square \tag{46}$$

K&K 3.6
In our first look at the ideal gas we considered only the translational energy of the particles. But molecules can rotate with kinetic energy. The rotational motion is quantized; and the energy levels of a diatomic molecule are of the form $\epsilon(j) = j(j+1)\epsilon_0$, where j is an positive integer including zero. The multiplicity of each rotational level is $g(j) = 2j + 1$.
Part a
Find the partition function $Z_R(\tau)$ for the rotational states of one molecule. Remember that Z is a sum over all states, not over all levels - this makes a difference.
The partition function will have the form

$$Z_R(\tau) = \sum_j (2j + 1)exp(-j(j+1)\epsilon_0/\tau) \quad \square \tag{47}$$

The sum over the states $\sum_s exp(-\epsilon_s/\tau)$ has been converted to a sum over the energy levels j via the degeneracy of the states $2j + 1$. For each j, there are $2j + 1$ states that share the same energy, so we must multiply by this factor to convert the sum over states into a sum over energy levels.
Part b

Evaluate $Z_R(\tau)$ approximately for $\tau \gg \epsilon_0$, by converting the sum to an integral.
We get, after converting the sum to an integral,

$$Z_R(\tau) = \int_{\frac{-1}{2}}^{\infty} dj(2j+1)exp(-j(j+1)\epsilon_0/\tau) \tag{48}$$

The lower limit on the integral is $-1/2$ since the function looks like a Gaussian, with zeroes at infinity and $j = -1/2$. Next, let $u = j(j+1)$. Then $(2j+1)dj = du$, and our integral is

$$Z_R(\tau) = \int_{\frac{-1}{4}}^{\infty} duexp(-u\epsilon_0/\tau) = -\frac{\tau}{\epsilon_0}exp(-u\epsilon_0/\tau)\Big|_{\frac{-1}{4}}^{\infty} = \frac{\tau}{\epsilon_0}exp(\epsilon_0/4\tau) \tag{49}$$

When $\tau \gg \epsilon_0$, the exponential dominates, we can expand the exponential to get:

$$Z_R(\tau) = \frac{\tau}{\epsilon_0}(1 + \frac{\epsilon_0}{4\tau} + ...) = \frac{\tau}{\epsilon_0} + \frac{1}{4} + O(\tau^{-1}) + ... \quad \square \tag{50}$$

Part c
Do the same for $\tau \ll \epsilon_0$, by truncating the sum after the second term.
Going back to equation 47 and taking only two terms, we get

$$Z_R(\tau) = \sum_{j=0}^{\infty}(2j+1)exp(-j(j+1)\epsilon_0/\tau) + ... = 1 + 3exp(-2\epsilon_0/\tau) + ... \quad \square \tag{51}$$

Part d
Give expressions for the energy U and the heat capacity C as functions of τ in both limits. Observe that the rotational contribution to the heat capacity of a diatomic molecule approaches 1 (or in conventional units k_B) when $\tau \gg \epsilon_0$.
U is related to the partition function by $U = \tau^2 \partial(lnZ)/\partial\tau$, so

$$U = \tau^2 \frac{\partial}{\partial\tau}\{ln(\frac{\tau}{\epsilon_0} + \frac{1}{4})\} = \frac{4\tau^2}{4\tau + \epsilon_0} \quad (\tau \gg \epsilon_0) \quad \square \tag{52}$$

and

$$C = \frac{\partial U}{\partial\tau} = \frac{\partial}{\partial\tau}(\frac{4\tau^2}{4\tau + \epsilon_0}) = \frac{8\tau(\epsilon_0 + 2\tau)}{(\epsilon_0 + 4\tau)^2} \propto \frac{16\tau^2}{16\tau^2} \approx 1 \quad (\tau \gg \epsilon_0) \quad \square \tag{53}$$

for the high temperature limit (from equation 50). For the low temperature limit, we have (from equation 51):

$$U = \tau^2 \frac{\partial}{\partial\tau}\{ln(1 + 3exp(-2\epsilon_0/\tau))\} = \frac{6\epsilon_0}{3 + exp(2\epsilon_0/\tau)} \approx 6\epsilon_0 exp(-2\epsilon_0/\tau) \quad (\tau \ll \epsilon_0) \quad \square \tag{54}$$

and

$$C = \frac{\partial U}{\partial\tau} = \frac{\partial}{\partial\tau}\{6\epsilon_0 exp(-2\epsilon_0/\tau)\} = \frac{12\epsilon_0^2}{\tau^2}exp(-2\epsilon_0/\tau) \quad (\tau \ll \epsilon_0) \quad \square \tag{55}$$

In the low temperature cases, the exponential terms dominate as $\tau \to 0$, so both the energy and heat capacity go to 0 as τ goes to 0.

K&K 3.7
A zipper has N links; each link has a state in which it is closed with energy 0 and a state in which it is open with energy ϵ. We require, however, the the zipper can only unzip from the left end, and that the link number s can only open if all links to the left $(1, 2, ...s - 1)$ are already open.
Part a
Show that the partition function can be summed in the form

$$Z = \frac{1 - exp[-(N+1)\epsilon/\tau]}{1 - exp(-\epsilon/\tau)} \tag{56}$$

The possible energies of the system are 0, if no links are open, ϵ, if 1 link is open, 2ϵ, if 2 links are open, etc, all the way up to $N\epsilon$, if all the links are open. Then the partition function is

$$Z = \sum_{n=0}^{N} exp(-n\epsilon/\tau) = \frac{1 - exp[-(N+1)\epsilon/\tau]}{1 - exp(-\epsilon/\tau)} \quad \square \tag{57}$$

where I have used the known formula for a finite geometric sum: $\sum_{s=0}^{N} x^s = (1 - x^{(N+1)})/(1 - x)$.

Part b

In the limit $\epsilon \gg \tau$, find the average number of open links. The model is a very simplified model of the unwinding of two-stranded DNA molecules.

The average number of open links is just the average energy of the system divided by ϵ, since the energy of the system is $U = \langle n \rangle \epsilon$ because closed links contribute 0 energy. The average energy can be evaluated as $U = 1/Z \sum_{n=0}^{N} n\epsilon x^n$, where x is the Boltzmann factor, or it can be calculated from the derivative of the logarithm of the partition function. In the low temperature limit, we can neglect the exponential term in the numerator, since it is already small, and since it is raised to the $N + 1$ power it is negligible compared to the denominator. So:

$$U = \tau^2 \frac{\partial lnZ}{\partial \tau} \approx -\tau^2 \frac{\partial}{\partial \tau} ln(1 - exp(-\epsilon/\tau)) = \frac{\epsilon}{1 - exp(-\epsilon/\tau)} \tag{58}$$

Therefore, the average number of open links is U/ϵ:

$$\langle n \rangle = \frac{1}{1 - exp(-\epsilon/\tau)} \quad \square \tag{59}$$

K&K 3.8

Consider one particle confined to a cube of side L; the concentration in effect is $n = 1/L^3$. Find the kinetic energy of the particle when in the ground orbital. There will be a value of the concentration for which this zero-point quantum kinetic energy is equal to the temperature τ. At this concentration the occupancy of the lowest orbital is of the order of unity; the lowest orbital always has a higher occupancy than any other orbital. Show that the concentration n_0 thus defined is equal to the quantum concentration $n_Q \equiv (m\tau/2\pi\hbar^2)^{3/2}$ within a factor of the order of unity.

The energy levels of a particle in a three dimensional box are

$$\epsilon = \frac{\hbar^2 \pi^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2) \equiv \epsilon_1(n_x^2 + n_y^2 + n_z^2) \tag{60}$$

In the ground state, $n_x = n_y = n_z = 1$ (remember, for a particle in a box, the quantum numbers can't be 0). Thus,

$$\epsilon = 3\epsilon_1 \quad \square \tag{61}$$

To find when this is equal to the temperature τ, we set $3\epsilon_1 = \tau$, or, in other words:

$$\frac{3\hbar^2 \pi^2}{2mL^2} = \tau \implies \frac{1}{L} = \sqrt{\frac{2m\tau}{3\hbar^2 \pi^2}} \tag{62}$$

and the concentration this corresponds to is

$$n_0 = \frac{1}{L^3} = (\frac{2m\tau}{3\hbar^2 \pi^2})^{3/2} = (\frac{4}{3\pi})^{3/2}(\frac{m\tau}{2\pi\hbar^2})^{3/2} = 0.28 n_Q \quad \square \tag{63}$$

K&K 3.9

Show that the partition function $Z(1+2)$ of two independent systems 1 and 2 in thermal contact at a common temperature τ is equal to the product of the partition functions of the separate systems: $Z(1+2)=Z(1)Z(2)$.

The partition function of two systems with energies ϵ_i and ϵ_j, respectively, are (since the combined energy is $\epsilon_i + \epsilon_j$):

$$Z(1+2) = \sum_i \sum_j exp(-(\epsilon_i + \epsilon_j)/\tau) = \sum_i exp(-\epsilon_i/\tau) \sum_j exp(-\epsilon_j/\tau) = Z(1)Z(2) \quad \square \tag{64}$$

K&K 3.10

The thermodynamic identity for a one-dimensional system is $\tau d\sigma = dU - f dl$, when f is the external force exerted on the line and dl is the extension of the line. We form the derivative to find:

$$-\frac{f}{\tau} = \left.\frac{\partial \sigma}{\partial l}\right|_U \tag{65}$$

The direction of the force is opposite to the conventional direction of the pressure. We consider a polymeric chain of N links each of length ρ, with each link equally likely to be directed to the right and to the left.

Part a

Show that the number of arrangements that give a head-to-tail length of $l = 2|s|\rho$ is

$$g(N, -s) + g(N, s) = \frac{2N!}{(\frac{N}{2} + s)!(\frac{N}{2} - s)!} \tag{66}$$

From equation 1.15,

$$g(N, s) = \frac{N!}{(\frac{N+2s}{2})!(\frac{N-2s}{2})!}, \quad g(N, -s) = \frac{N!}{(\frac{N-2s}{2})!(\frac{N+2s}{2})!} \tag{67}$$

Adding them yields:

$$g(N, -s) + g(N, s) = \frac{2N!}{(\frac{N}{2} + s)!(\frac{N}{2} - s)!} \quad \square \tag{68}$$

Part b

For $|s| \ll N$ show that

$$\sigma(l) = ln[2g(N, 0)] - l^2/2N\rho^2 \tag{69}$$

We use equation 1.35 in K&K

$$g(N, -s) + g(N, s) = 2g(N, 0)exp(-2s^2/N) \tag{70}$$

and the entropy is the logarithm of this:

$$\sigma = ln(g(N, -s) + g(N, s)) = ln(2g(N, 0)) - 2s^2/N \tag{71}$$

and letting $s = l/2\rho$, we get:

$$\sigma = ln(2g(N, 0)) - l^2/2N\rho^2 \quad \square \tag{72}$$

Part c

Show that the force at an extension l is

$$f = l\tau/N\rho^2 \tag{73}$$

The force is proportional to the temperature. The force arises because the polymer wants to curl up: the entropy is higher in a random coil that in an uncoiled configuration. Warming a rubber band makes it contract; warming a steel wire makes it expand.

This is a simple application of equation 65. We will take the derivative of the entropy (equation 72) with respect to l:

$$f = -\tau \left.\frac{\partial \sigma}{\partial l}\right|_U = \tau \frac{l}{N\rho^2} \quad \square \tag{74}$$

K&K 3.11

Consider an ideal gas of N particles, each of mass M, confined to a one-dimensional line of length L. Find the entropy at temperature τ. The particles have spin 0.

These particles have the energies of a particle in a box: $\epsilon = n^2\pi^2\hbar^2/2mL^2$, so the partition function is

$$Z = \frac{1}{N!}\prod_{i=0}^{N}\int_0^\infty dn\, exp(-n^2\pi^2\hbar^2/2\tau m_i L^2) = (\sqrt{\frac{\tau m}{2\pi\hbar^2}}L)^N/N! \equiv \frac{Z_1^N}{N!} \tag{75}$$

where the $N!$ comes from the indistinguishability of the particles and the product is over each particle. Since the partition functions are identical (the masses of the particles are the same), the result can simply be raised to the Nth power.

From here, we use $\sigma = \partial F/\partial\tau$, with $F = -\tau ln(Z)$ to get the entropy:

$$F = -\tau ln(\frac{Z_1^N}{N!}) = -\tau N ln(L) - \tau N ln(\sqrt{\frac{m}{2\pi\hbar^2}}) - \tau\frac{N}{2}ln(\tau) + \tau N ln(N) - \tau N \tag{76}$$

where I have substituted in the one particle partition function from equation 75. So the entropy is

$$\sigma = \frac{\partial F}{\partial\tau} = N[ln\{n(\frac{2\pi\hbar^2}{m\tau})^{3/2}\} - 3/2] \quad \square \tag{77}$$

K&K 4.1

Show that the number of photons $\sum\langle s_n\rangle$ in equilibrium at temperature τ in a cavity of volume V is

$$N = 2.404\pi^{-2}V(\tau/\hbar c)^3 \tag{78}$$

From equation 23 in K&K the entropy is $\sigma = 4\pi^2V/45)(\tau/\hbar c)^3$, whence $\sigma/N \approx 3.602$. It is believed that the total number of photons in the universe is 10^8 times larger than the total number of nucleons (protons, neutrons). Because both entropies are of the order of the respective number of particles (see equation 3.76 in K&K), the photons provide the dominant contribution to the entropy of the universe, although the particles dominate the total energy. We believe that the entropy of the photons is essentially constant, so that the entropy of the universe is approximately constant with time.

We need to calculate

$$n_{photons} = \sum_n\langle s_n\rangle = \sum_n\frac{1}{exp(\hbar\omega_n/\tau) - 1} \tag{79}$$

where ω_n is derived in the book to be $n\pi c/L$. To do this, we convert the sum to an integral and say that the modes are approximately continuous. Furthermore, the modes n can be a combination of n_x or n_y so we need to integrate over $2\times 1/8\times d^3n = 2\times 1/8\times 4\pi n^2 dn$, where the 2 comes from the two polarizations of the photon, and the 1/8 comes from the 1/8 (octant) of the sphere.

$$n_{photons} = \int_0^\infty\frac{1}{exp(\hbar n\pi c/L\tau) - 1}\pi n^2 dn = \frac{V\tau^3}{\hbar^3\pi^2 c^3}\int_0^\infty\frac{u^2}{exp(u) - 1}du \tag{80}$$

where $V = L^3$, after a simple u substitution. The integral is just a product of the gamma and zeta functions:

$$n_{photons} = \frac{V\tau^3}{\hbar^3\pi^2 c^3}\Gamma(3)\zeta(3) = 2.404\frac{V\tau^3}{\hbar^3\pi^2 c^3} \quad \square \tag{81}$$

where I have used the fact that $\Gamma(3) = 2$ and $\zeta(3) = 1.202$.

K&K 4.2

The value of the total radiant energy flux density at the Earth from the Sun is called the *solar constant* **of the Earth. The observed value integrated over all emission wavelengths and referred to the mean Earth-Sun distance is**

$$solar\ constant = 0.136\ Js^{-1}cm^{-2} \tag{82}$$

Part a
Show that the total rate of energy generation of the Sun is $4 \times 10^{26} Js^{-1}$.
By dimensionality, we can see that we need to multiply the solar constant by an area. Why? The energy generated on the Sun is radiated in all directions, and the intensity (energy flux density) observed at a distance d from the Sun will be smaller the larger d is. We multiply the intensity (solar constant) by the area of the spherical shell of energy flux that is hitting the Earth.

$$P_{Sun} = 0.136 \times 4\pi d_{Sun-Earth}^2 = 0.136 \times 4\pi (1.5 \times 10^{13})^2 = 4 \times 10^{26} \; Js^{-1} \quad \square \tag{83}$$

Part b
From this result and Stefan's law, the energy flux density $J_U = 5.67 \times 10^{-12} Js^{-1} cm^{-2}$; show that the effective temperature of the surface of the Sun treated as a black body is $T \approx 6000K$. Take the distance of the Earth from the sun as $1.5 \times 10^{13} cm$ and the radius of the Sun as $7 \times 10^{10} cm$.
The power radiated per area is given by P_{Sun}/A_{Sun}:

$$P_{radiated/area} = \frac{P_{Sun}}{A_{Sun}} = \frac{4 \times 10^{26}}{4\pi \times (7 \times 10^{10})^2} = 6.2 \times 10^3 Js^{-1} cm^{-2} \tag{84}$$

and then by Stefan's law, we can relate the power radiated per unit area (i.e. the flux F) to the temperature via $F = \sigma T^4$, where σ is Stefan's constant equal to $5.67 \times 10^{-12} Js^{-1} cm^{-2} K^{-4}$:

$$F = \sigma T^4 \quad \Rightarrow \quad T = (\frac{6.2 \times 10^3}{5.67 \times 10^{-12}})^{1/4} = 5750K \quad \square \tag{85}$$

K&K 4.3
Part a
Estimate by a dimensional argument or otherwise the order of magnitude of the gravitational self-energy of the Sun, $M_{Sun} = 2 \times 10^{33} g$, $R_{Sun} = 7 \times 10^{10} cm$, $G = 6.6 \times 10^{-8} \; dyne \; cm^2 \; g^{-2}$.
The self-energy has units of $erg = dyne \cdot cm$. Furthermore, by convention it is negative. The correct combination of the mass, radius, and gravitational constant is (and hopefully you remember this equation from introductory physics):

$$U_{g.s.e.} = -\frac{GM_{Sun}^2}{R_{Sun}} = -\frac{6.6 \times 10^{-8} \; dyne \; cm^2 \; g^{-2} (2 \times 10^{33} g)^2}{7 \times 10^{10} cm} = -3.77 \times 10^{48} ergs \quad \square \tag{86}$$

Part b
Assume that the total thermal kinetic energy of the atoms in the Sun is equal to -1/2 the gravitational self-energy. Estimate the average temperature of the Sun, assuming that there are 1×10^{57} particles.
This means that the thermal kinetic energy of particles in the Sun is $U_{thermal} \approx -2 \times 10^{48} ergs$. We will assume that the Sun is composed entirely of Hydrogen (not a bad assumption), which is a monatomic particle. Therefore, we can relate the thermal energy to the temperature via the equipartition theorem:

$$U_{thermal} = \frac{3}{2} N k_B T \quad \Rightarrow \quad T = \frac{2U_{thermal}}{3Nk_B} = \frac{-4 \times 10^{48} erg}{3 \times 10^{57} \times 1.38 \times 10^{-16} erg \; K^{-1}} = 9 \times 10^6 K \quad \square \tag{87}$$

K&K 4.4
Suppose $4 \times 10^{26} Js^{-1}$ is the total rate at which the Sun radiates energy at the present time.
Part a
Find the total energy of the Sun available for radiation, on the rough assumptions that the energy source is the conversion of hydrogen (atomic weight 1.0078) to helium (4.0026) and that the reaction stops when 10 percent of the original hydrogen has

been converted to helium. Use the Einstein relation $E = \Delta M c^2$.

The Sun consists of $M_{Sun}/M_{Hydrogen} = 2 \times 10^{30} kg / 1.67 \times 10^{-27} kg \approx 1 \times 10^{57}$ Hydrogen atoms. That means that the reaction stops when 1×10^{56} Hydrogen atoms have been converted to Helium. Now, it takes 4 Hydrogen atoms to make 1 Helium. So:

$$\Delta M = (4 \times 1.0078 - 1 \times 4.0026) \times 10^{56} \approx 3 \times 10^{54} amu = 5 \times 10^{27} kg \tag{88}$$

That means that the total energy of the Sun available for radiation is

$$E = \Delta M c^2 \approx 4.5 \times 10^{44} J \quad \square \tag{89}$$

Part b
Use (a) to estimate the life expectancy of the Sun. It is believed that the age of the Universe is about 10×10^9 years.
Power radiated is $4 \times 10^{26} Js^{-1}$, so the total time that it will take to radiate the amount of energy given in equation 89 is

$$t = \frac{E}{P} = \frac{4.5 \times 10^{44} J}{4 \times 10^{26} Js^{-1}} \approx 10^{18} s = 3 \times 10^{10} yr \quad \square \tag{90}$$

K&K 4.5
Calculate the temperature of the surface of the Earth on the assumption that as a black body in thermal equilibrium it reradiates as much thermal radiation as it receives from the Sun. Assume also that the surface of the Earth is at a constant temperature over the day-night cycle. Use $T_{Sun} = 5800K; R_{Sun} = 7 \times 10^{10} cm; d_{Earth-Sun} = 1.5 \times 10^{13} cm$.
The power emitted by the Sun is the flux of the Sun (which can be obtained from Boltzmann's law) multiplied by the surface area of the sphere over which the power is emitted (the area of the surface of the Sun). The power is therefore:

$$P_{Sun} = F_{Sun} A_{Sun} = \sigma T_{Sun}^4 4\pi R_{Sun}^2 \tag{91}$$

Meanwhile, the flux density that hits the earth is the power emitted by the Sun divided by the surface area of the sphere over the which the power spreads out. The flux should be smaller at the Earth then at the Sun.

$$F_{at\ Earth} = \frac{P_{Sun}}{4\pi d_{Sun-Earth}^2} = \frac{\sigma T_{Sun}^4 R_{Sun}^2}{d_{Sun-Earth}^2} \tag{92}$$

This means that the total flux is $F_{at\ Earth}$ times the cross sectional area of the Earth ($\Phi_{in} = F_{at\ Earth} \pi R_{Earth}^2$). Since we are assuming that the Earth reradiates all of this flux, we know that the flux is radiated out over the entire surface area of the Earth ($\Phi_{out} = \sigma T_{Earth}^4 4\pi R_{Earth}^2$). Equating Φ_{in} and Φ_{out} gives:

$$\sigma T_{Earth}^4 4\pi R_{Earth}^2 = \pi R_{Earth}^2 \frac{\sigma T_{Sun}^4 R_{Sun}^2}{d_{Sun-Earth}^2} \quad \Rightarrow \quad T_{Earth} = \sqrt{\frac{R_{Sun}}{2 d_{Sun-Earth}}} T_{Sun} \approx 280K \quad \square \tag{93}$$

K&K 4.6
Show for a photon gas that:
Part a

$$p = -\left.\frac{\partial U}{\partial V}\right|_\sigma = -\sum_j s_j \hbar \frac{d\omega_j}{dV} \tag{94}$$

where s_j is the number of photons in mode j.
We know that $U = \sum_j s_j \hbar \omega_j$. We can plug that into equation 94 to obtain:

$$p = -\frac{\partial}{\partial V} \sum_j s_j \hbar \omega_j = -\sum_j \left.\frac{\partial s_j}{\partial V}\right|_\sigma \hbar \omega_j - \sum_j s_j \hbar \left.\frac{\partial \omega_j}{\partial V}\right|_\sigma \tag{95}$$

But $\partial s_j / \partial V$ must vanish, since otherwise the state itself would change (since the occupation number changes) with a change in volume, and we require that an isentropic change keep the same state. Therefore,

$$p = -\sum_j s_j \hbar \frac{d\omega_j}{dV}\bigg|_\sigma \quad \square \tag{96}$$

where the partial derivative has been changed to a full derivative because the mode frequencies depend only on the cavity's dimensions.

Part b

Show for a photon gas that:

$$\frac{d\omega_j}{dV} = -\frac{\omega_j}{3V} \tag{97}$$

The frequency of the modes is related to the wavenumber by a linear dispersion relation, $\omega_j = ck_j$. Since the modes are confined to a box of volume $L \times L \times L = V$, we know (e.g. the particle in a box) that the wavenumber must be an integer multiple of π/L, i.e. $k_j = n_j \pi / L$, and therefore the frequencies are $\omega_j = n_j c\pi / L$. Plugging this into equation 97, we get

$$\frac{dn_j c\pi / L}{dV} = n_j c\pi \frac{d}{dV} V^{-1/3} = -\frac{n_j c\pi}{3} V^{-4/3} = -\frac{\omega_j}{3V} \quad \square \tag{98}$$

Part c

Show for a photon gas that:

$$p = \frac{U}{3V} \tag{99}$$

This follows directly from equations 96 and 98, and the fact that $U = \sum_j s_j \hbar \omega_j$. Since the volume doesn't depend on which state the system is in, we can pull $3V$ out of the sum in expression 96, and recognizing the remaiening part as the internal energy U, we have

$$p = \frac{U}{3V} \quad \square \tag{100}$$

Thus the radiation pressure is equal to a third of the energy density.

Part d

Compare the pressure of thermal radiation with the kinetic pressure of a gas of H atoms at a concentration of 1 mole cm^{-3} characteristic of the Sun. At what temperature (roughly) are the two pressures equal? The average temperature of the Sun is believed to be near 2×10^7 K. The concentration is highly nonuniform and rises to near 100 mole cm^{-3} at the center, where the kinetic pressure is considerably higher than the radiation pressure.

For a hydrogen gas, which we will model as an ideal gas, $p = nRT/V$. For photons, the pressure is

$$p = \frac{\pi^2 k_B^4}{45\hbar^3 c^3} T^4 \tag{101}$$

So we can set the hydrogen and photon pressures equal to each other:

$$\frac{nRT}{V} = \frac{\pi^2 k_B^4}{45\hbar^3 c^3} T^4 \quad \Rightarrow \quad T = \sqrt[3]{\frac{45\hbar^3 c^3 nR}{\pi^2 k_B^4 V}} \approx 3.2 \times 10^7 K \quad \square \tag{102}$$

This means that in the Sun, where the average temperature is lower than $3.2 \times 10^7 K$, the kinetic pressure due to the hydrogen atoms is greater than the pressure of thermal radiation.

K&K 4.7

Part a

Show that the partition function of a photon gas is given by

$$Z = \prod_n [1 - exp(-\hbar \omega_n / \tau)]^{-1} \tag{103}$$

where the product is over the modes n.

The partition function for a single mode with frequency ω_n is determined by looking at the energies: $E = n\hbar\omega_n$. The partition function of a single photon mode is then

$$Z_1 = \sum_{n=0}^{\infty} exp(-n\hbar\omega_n/\tau) = \frac{1}{1 - exp(-\hbar\omega_n/\tau)} \tag{104}$$

However, the different modes are independent of each other. The partition function for all the modes in the box is the product of the partition functions for each mode ($Z_{total} = Z_1 Z_2 ... Z_n$). Therefore,

$$Z = \prod_n [1 - exp(-\hbar\omega_n/\tau)]^{-1} \quad \square \tag{105}$$

Part b
The Helmholtz free energy is found directly from equation 103 as

$$F = \tau \sum_n ln[1 - exp(-\hbar\omega_n/\tau)] \tag{106}$$

Transform the sum into an integral; integrate by parts to find

$$F = -\frac{\pi^2 V \tau^4}{45\hbar^3 c^3} \tag{107}$$

As before, the sum transforms to an integral via

$$\sum_n \rightarrow 2 \times \frac{1}{8} \times 4\pi \int_0^{\infty} n^2 dn = \pi \int_0^{\infty} n^2 dn \tag{108}$$

Copying from problem 4.6: The frequency of the modes is related to the wavenumber by a linear dispersion relation, $\omega_n = ck_n$. Since the modes are confined to a box of volume $L \times L \times L = V$, we know (e.g. the particle in a box) that the wavenumber must be an integer multiple of π/L, i.e. $k_n = n\pi/L$, and therefore the frequencies are $\omega_n = nc\pi/L$. Then equation 106 becomes

$$F = \pi\tau \int_0^{\infty} ln(1 - exp(-\hbar cn\pi/L\tau)n^2 dn \tag{109}$$

Now let $u = \hbar cn\pi/L\tau$, leading to

$$F = \frac{L^3 \tau^4}{\hbar^3 c^3 \pi^2} \int_0^{\infty} ln(1 - exp(-u))u^2 du \tag{110}$$

Integrating by parts, with $ln(1 - exp(-u)) = y$ and $u^2 du = dv$, we get

$$F = \frac{L^3 \tau^4}{\hbar^3 c^3 \pi^2} ln(1 - exp(-u))\frac{u^3}{3}\Big|_0^{\infty} - \frac{L^3 \tau^4}{3\hbar^3 c^3 \pi^2} \int_0^{\infty} \frac{u^3}{exp(u) - 1} du \tag{111}$$

Carefully using L'Hopital's rule on the first term, we can see that both limits go to 0. As for the second integral, it's value is $\Gamma(4)\zeta(4) = 6 \times \pi^4/90 = \pi^4/15$. So, finally, writing $L^3 \equiv V$, we obtain

$$F = -\frac{\pi^2 V \tau^4}{45\hbar^3 c^3} \quad \square \tag{112}$$

K&K 4.8
A black (non reflective) plane at temperature T_u is parallel to a black plane at temperature T_l. The net energy flux density in vacuum between the two planes is $J_U = \sigma_B(T_u^4 - T_l^4)$, where σ_B is the Stefan-Boltzmann constant. A third black plane is inserted between the other two and is allowed to come to a steady state temperature T_m. Find T_m in terms of T_u and T_l, and show that the net energy flux density is cut in half because of the presence of this plane. This is the principle of the heat shield

and is widely used to reduce the radiant heat transfer. *Comment:* **The result for N independent heat shields floating in temperature between the planes T_u and T_l is that the net energy flux density is $J_U = \sigma_B(T_u^4 - T_l^4)/(N+1)$.**

Let's look at the general case, where we have N planes at temperatures $T_1, T_2, ..., T_{N+1}$. The energy flux density between planes n and $n-1$ is is $J_U = \sigma_B(T_n^4 - T_{n-1}^4)$, and therefore

$$T_n^4 = T_{n-1}^4 + \frac{J_U}{\sigma_B} \tag{113}$$

The flux between any two planes needs to be the same, otherwise some of the planes would not be in equilibrium. So we can equally well write down an expression for T_{n-1}^4:

$$T_{n-1}^4 = T_{n-2}^4 + \frac{J_U}{\sigma_B} \tag{114}$$

and similarly for T_{n-2}^4, etc. So:

$$T_n^4 = T_{n-m}^4 + m\frac{J_U}{\sigma_B} = T_l^4 + n\frac{J_U}{\sigma_B} \tag{115}$$

In particular, if $T_{N+1} \equiv T_u$ and $T_{n-m} \equiv T_l$, then

$$T_u^4 = T_l^4 + (N+1)\frac{J_U}{\sigma_B} \quad \Rightarrow \quad J_U = \frac{\sigma_B(T_u^4 - T_l^4)}{N+1} \tag{116}$$

and inserting this into equation 115 yields

$$T_n^4 = \frac{(N+1-n)T_l^4 + nT_u^4}{N+1} \tag{117}$$

and the particular case of $n = N = 1$ yields

$$J_U = \sigma_B\frac{T_u^4 - T_l^4}{2}, \quad T_1^4 = \frac{T_l^4 + T_u^4}{2} \quad \square \tag{118}$$

K&K 4.10
Intergalactic space is believed to be occupied by hydrogen atoms in a concentration ≈ 1 *atom* m^{-3}. The space is also occupied by thermal radiation at 2.9K, from the Primitive Fireball. Show that the ratio of the heat capacity of matter to that of radiation is $\approx 10^{-9}$.

The internal energy of hydrogen atoms, modeled as an ideal gas, is well known to be $U = 3/2n\tau$, meaning that the heat capacity (per unit volume) is

$$C_{matter} = \frac{3}{2}n \tag{119}$$

Meanwhile for photons, the internal energy was derived in K&K by calculating $U = \sum_n \langle s \rangle \hbar\omega_n = \sum_n \hbar\omega_n/[exp(\hbar\omega_n/\tau) - 1]$. The sum was converted to an integral via the method discussed in problems 4.6 and 4.8. The internal energy of photons is therefore:

$$U = \frac{\pi^2 V \tau^4}{15\hbar^3 c^3} \tag{120}$$

Alternatively, the internal energy could be found by calculating $U = \tau^2 \partial(lnZ)/\partial\tau$ for the partition function in problem 4.7. From this we can easily calculate the heat capacity per unit volume of photons to be:

$$C_\gamma = \frac{4\pi^2\tau^3}{15\hbar^3 c^3} \tag{121}$$

Therefore, the ratio of the matter heat capacity to the photon heat capacity is

$$\frac{C_{matter}}{C_\gamma} = \frac{45n\hbar^3 c^3}{8\pi^2 k_B^3 T^3} \approx 2.8 \times 10^{-10} \quad \square \tag{122}$$

K&K 5.1
Centrifuge: A circular cylinder of radius R rotates about the long axis with angular velocity ω. The cylinder contains an ideal gas of atoms of mass M at temperature τ. Find an expression for the dependence of the concentration $n(r)$ on the radial distance r from the axis, in terms of $n(0)$ on the axis. Take μ as for an ideal gas.
The potential energy corresponding to the centrifugal motion is $-M\omega^2 r^2/2$, which serves as the external chemical potential. Now, the internal chemical potential of an ideal gas is

$$\mu = \tau ln[\frac{n(r)}{n_Q}] \tag{123}$$

where n_Q is the particle concentration (i.e. the number of particles per unit volume) of a system where the inter particle distance is equal to the thermal de Broglie wavelength ($Z_{ideal-gas} = n_Q V$). Now, this means that the total chemical potential is

$$\mu_{total} = \tau ln[\frac{n(r)}{n_Q}] - \frac{1}{2}M\omega^2 r^2 \tag{124}$$

For the ideal gas to be in equilibrium, the chemical potential must be independent of radial distance:

$$\tau ln[\frac{n(r)}{n_Q}] - \frac{1}{2}M\omega^2 r^2 = \tau ln[\frac{n(0)}{n_Q}] \tag{125}$$

Solving for the concentration as a function of radial distance:

$$n(r) = n(0)exp(M\omega^2 r^2/2\tau) \quad \square \tag{126}$$

K&K 5.2
Molecules in the Earth's atmosphere: If n is the concentration of molecules at the surface of the Earth, M the mass of a molecule, and g the gravitational acceleration at the surface, show that at constant temperature, the total number of molecules in the atmosphere is

$$N = 4\pi n(R)exp(-MgR/\tau) \int_R^\infty drr^2 exp(MgR^2/r\tau) \tag{127}$$

with r measured from the center of the Earth; here R is the radius of the Earth. The integral diverges at the upper lmit, so that N cannot be bounded and the atmosphere cannot be in equilibrium. Molecules, particularly light molecules, are always escaping from the atmosphere.
The potential energy of a molecule in Earth's gravitational field (taken at a distance r from the center of the Earth) is $U = -MgR^2/r$. Here, this will act as an external chemical potential. The total chemical potential is, then,

$$\mu(r) = \tau ln[\frac{n(r)}{n_Q}] - \frac{MgR^2}{r} \tag{128}$$

At diffuse equilibrium, the chemical potential is independent of r, so that, for instance, the chemical potential at a height r from the center of the Earth will be equal to the chemical potential at a distance R from the center of the Earth:

$$\tau ln[\frac{n(r)}{n_Q}] - \frac{MgR^2}{r} = \tau ln[\frac{n(R)}{n_Q}] - MgR \tag{129}$$

from which follows that

$$n(r) = n(R)exp(-MgR/\tau)exp(MgR^2/r\tau) \tag{130}$$

and so the total number of molecules in the atmosphere is (we integrate from R in order to only include the atmosphere and not the interior of the Earth):

$$N = \int n(r)d^3r = 4\pi n(R)exp(-MgR/\tau)\int_R^\infty dr r^2 exp(MgR^2/r\tau) \quad \Box \tag{131}$$

the caveat of constant temperature allows us to pull the first exponential through the integral.

K&K 5.3

Potential energy of a gas in a gravitational field: Consider a column of atoms each of mass M at temperature τ in a uniform gravitational field g. Find the thermal average potential energy per atom. The thermal average kinetic energy density is independent of height. Find the total heat capacity per atom. The total heat capacity is the sum of contributions from the kinetic energy and from the potential energy. Take the zero of the gravitational energy at the bottom $h = 0$ of the column. Integrate from $h = 0$ to $h = \infty$.

We know from the equipartition theorem that the total thermal *kinetic* energy is $U_k = 3N\tau/2$. We need to find the total thermal potential energy. The total potential energy is determined via $U_{pot} = \int n(h)U_{pot}(h)dh$. What are n(h) and U(h)? U(h) we remember from introductory physics to be mgh. To find n(h), let's equate the total chemical potentials (internal+external) at a height h and at a height $h = 0$:

$$\tau ln[\frac{n(h)}{n_Q}] + Mgh = \tau ln[\frac{n(0)}{n_Q}] \quad \Rightarrow \quad n(h) = n(0)exp(-Mgh/\tau) \tag{132}$$

Therefore the total potential energy is

$$U_{pot} = Mgn(0)\int_0^\infty he^{-Mgh/\tau}dh = \frac{n(0)\tau^2}{Mg} \tag{133}$$

But we want to put this in terms of the total number of particles N.

$$N = \int_0^\infty n(h)dh = \int_0^\infty n(0)exp(-Mgh/\tau)dh = \frac{n(0)\tau}{Mg} \tag{134}$$

So we can write the potential energy in equation 133 as

$$U_{pot} = N\tau \tag{135}$$

So the thermal average potential energy per atom is τ. $\Box$

Therefore the total energy is

$$E = U_k + U_{pot} = \frac{5}{2}N\tau \tag{136}$$

which makes the total heat capacity per atom is

$$\frac{C}{N} = \frac{\partial(E/N)}{\partial\tau} = \frac{5}{2} \quad \Box \tag{137}$$

K&K 5.6

Part a

Consider a system that may be unoccupied with energy zero or occupied by one particle in either of two states, one of energy zero and one of energy ϵ. Show that the Gibbs sum for this system is

$$\mathcal{Z} = 1 + \lambda + \lambda exp(-\epsilon/\tau). \tag{138}$$

($\lambda = exp(\mu/\tau)$). **Our assumption excludes the possibility of one particle in each state at the same time. Notice that we include in the sum a term for $N = 0$ as a particular state of a system of a variable number of particles.**

The Gibbs sum is

$$\mathcal{Z} = \sum_n \sum_{s(n)} exp((n\mu - \epsilon_{s(n)}/\tau) \tag{139}$$

Let's first sum over the energies. There are only two possible ones, 0 and ϵ, so the Gibbs sum becomes

$$\mathcal{Z} = \sum_n exp(n\mu/\tau) + \sum_{n\neq 0} exp((n\mu - \epsilon)/\tau) \tag{140}$$

Now we can sum over the particles. There is only one particle, but we sum from $n = 0$ to $n = 1$:

$$\mathcal{Z} = 1 + exp(\mu/\tau) + exp((\mu - \epsilon))/\tau) \tag{141}$$

Notice that the term $exp(-\epsilon/\tau)$ is not there. I have put a restriction on n in the second sum in equation 140. The reason for this is that we must have three terms in the Gibbs function, since there are three possible states. Furthermore, that term corresponds to a state which is unoccupied, but still has a nonzero energy, which is unphysical. Think about it. The 1 corresponds to the unoccupied case ($n = 0, \epsilon_n = 0$). The second term corresponds to the case where the state is occupied but with zero energy ($n = 1, \epsilon_n = 0$). The third term corresponds to the state which is occupied with nonzero energy ($n = 1, \epsilon_n = \epsilon$). So, finally, writing everything in terms of λ:

$$\mathcal{Z} = 1 + \lambda + \lambda exp(-\epsilon/\tau) \quad \square \tag{142}$$

Part b
Show that the thermal average occupancy of the system is

$$\langle N \rangle = \frac{\lambda + \lambda exp(-\epsilon/\tau)}{\mathcal{Z}} \tag{143}$$

We can write the definition of the thermal average occupancy:

$$\langle N \rangle = \frac{1}{\mathcal{Z}} \sum_n \sum_{s(n)} n \, exp((n\mu - \epsilon_{s(n)}))/\tau) \tag{144}$$

and look at the three states individually. The first state has $n = 0, \epsilon_n = 0$, so it doesn't contribute to the sum (since $n = 0$). The second has $n = 1, \epsilon_n = 0$, while the third has $n = 1, \epsilon_n = \epsilon$. We therefore write out the expression 144:

$$\langle N \rangle = \frac{1}{\mathcal{Z}}(\lambda + \lambda exp(-\epsilon/\tau)) \quad \square \tag{145}$$

Show that the thermal average occupancy of the state at energy ϵ is

$$\langle N(\epsilon) \rangle = \frac{\lambda exp(-\epsilon/\tau)}{\mathcal{Z}} \tag{146}$$

The first term in equation 145 corresponds to the thermal average occupancy of the state with energy 0, while the second term is what we need: the thermal average occupancy of the state at energy ϵ:

$$\langle N(\epsilon) \rangle = \frac{\lambda exp(-\epsilon/\tau)}{\mathcal{Z}} \quad \square \tag{147}$$

Part d
Find an expression for the thermal average energy of the system.
We can write the definition of the thermal average energy:

$$\langle \epsilon \rangle = \frac{1}{\mathcal{Z}} \sum_n \sum_{s(n)} \epsilon_n \, exp((n\mu - \epsilon_{s(n)}))/\tau) \tag{148}$$

Of course, the state with $\epsilon_n = 0$ do not contribute to the sum, so we are left with the state with $n = 1, \epsilon_n = \epsilon$:

$$\langle \epsilon \rangle = \frac{1}{\mathcal{Z}} \epsilon \lambda exp(-\epsilon/\tau) \quad \square \tag{149}$$

which is, not coincidentally, equal to $\epsilon \langle N(\epsilon) \rangle$.

Part e

Allow the possibility that the orbital at 0 and at ϵ may be occupied each by one particle at the same time; show that

$$\mathcal{Z} = 1 + \lambda + \lambda exp(-\epsilon/\tau) + \lambda^2 exp(-\epsilon/\tau) = (1 + \lambda)[1 + \lambda exp(-\epsilon/\tau)]. \tag{150}$$

Because $\mathcal{Z}$ can be factored as shown, we have in effect two independent systems.
Going back to equation 140, we can make the change that there is now a state with occupancy $N = 2$ and energy $\epsilon + 0 = \epsilon$:

$$\mathcal{Z} = \sum_{n=0}^{1} exp(n\mu/\tau) + \sum_{n \neq 0}^{2} exp((n\mu - \epsilon)/\tau) \tag{151}$$

which is evaluated in terms of λ as

$$\mathcal{Z} = 1 + \lambda + \lambda exp(-\epsilon/\tau) + \lambda^2 exp(-\epsilon/\tau) = (1 + \lambda)[1 + \lambda exp(-\epsilon/\tau)] \quad \square \tag{152}$$

This has the form $\mathcal{Z} = \mathcal{Z}_0 \mathcal{Z}_\epsilon$ of the Gibbs sum for two independent systems, one with no energy regardless of occupancy, and the other with energy 0 or ϵ if it is empty or has occupancy 1, respectively. Both systems can be either unoccupied or occupied by just one particle, but the crucial point is that the occupancies of both systems are entirely independent of each other.

K&K 5.7

States of positive and negative ionization: Consider a lattice of fixed hydrogen atoms; suppose that each atom can exist in four states: Ground: $n_e = 1$, $\epsilon = -\Delta/2$, Positive ion state: $n_e = 0$, $\epsilon = -\delta/2$, Negative ion state: $n_e = 2$, $\epsilon = \delta/2$, and excited state: $n_e = 1$, $\epsilon = \Delta/2$. Find the condition that the average number of electrons $\langle n_e \rangle$ per atom be unity. The condition will involve δ, λ, and τ.

We need to write down the Gibbs sum for this system. The ground state has Gibbs factor

$$\mathcal{Z}_g = exp((\mu + \Delta/2)/\tau) \tag{153}$$

The positive ion state has Gibbs factor

$$\mathcal{Z}_+ = exp((\delta/2)/\tau) \tag{154}$$

The negative ion state has Gibbs factor

$$\mathcal{Z}_- = exp((2\mu - \delta/2)/\tau) \tag{155}$$

The excited state has Gibbs factor

$$\mathcal{Z}_e = exp((\mu - \Delta/2)/\tau) \tag{156}$$

meaning that the Gibbs sum is

$$\mathcal{Z} = exp((\mu + \Delta/2)/\tau) + exp((\delta/2)/\tau) + exp((2\mu - \delta/2)/\tau) + exp((\mu - \Delta/2)/\tau) \tag{157}$$

or in terms of the absolute activity λ:

$$\mathcal{Z} = \lambda exp(\Delta/2\tau) + exp(\delta/2\tau) + \lambda^2 exp(-\delta/2\tau) + \lambda exp(-\Delta/2\tau) \tag{158}$$

Now we can write down $\langle N \rangle$:

$$\langle N \rangle = \frac{1 \times \lambda exp(\Delta/2\tau) + 0 \times exp(\delta/2\tau) + 2 \times \lambda^2 exp(-\delta/2\tau) + 1 \times \lambda exp(-\Delta/2\tau)}{\lambda exp(\Delta/2\tau) + exp(\delta/2\tau) + \lambda^2 exp(-\delta/2\tau) + \lambda exp(-\Delta/2\tau)} \tag{159}$$

we want this to equal unity:

$$\langle N \rangle = \frac{\lambda exp(\Delta/2\tau) + 2\lambda^2 exp(-\delta/2\tau) + \lambda exp(-\Delta/2\tau)}{\lambda exp(\Delta/2\tau) + exp(\delta/2\tau) + \lambda^2 exp(-\delta/2\tau) + \lambda exp(-\Delta/2\tau)} = 1 \tag{160}$$

which leads immediately to

$$\lambda^2 = exp(\delta/\tau) \quad \Rightarrow \quad \mu = \delta/2 \quad \square \tag{161}$$

if we recall the definition of λ as $\lambda = exp(\mu/\tau)$.

K&K 5.11
Equivalent definition of chemical potential: The chemical potential was defined in K&K as

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{\tau,V} \tag{162}$$

An equivalent expression is

$$\mu = \left. \frac{\partial U}{\partial N} \right|_{\sigma,V} \tag{163}$$

Prove that this relation, which was used by Gibbs to define μ, is equivalent to the definition (162) that we have adopted. It will be convenient to make use of the results

$$d\sigma = \left. \frac{\partial \sigma}{\partial U} \right|_{V,N} dU + \left. \frac{\partial \sigma}{\partial V} \right|_{U,N} dV + \left. \frac{\partial \sigma}{\partial N} \right|_{U,V} dN \tag{164}$$

and

$$\mu = -\tau \left. \frac{\partial \sigma}{\partial N} \right|_{U,V} \tag{165}$$

Our reasons for treating equation 162 as the definition of μ and 163 as a mathematical consequence, are two-fold. In practice, we need the chemical potential more often as a function of the temperature τ than as a function of the entropy σ. Operationally, a process in which a particle is added to a system while the temperature of the system is kept constant is a more natural process than one in which the entropy is kept constant: Adding a particle to a system at a finite temperature tends to increase its entropy unless we can keep each system of the ensemble in a definite, although new, quantum state. There is no natural laboratory process by which this can be done. Hence the definition 162 in which the chemical potential is expressed as the change in free energy per added particle under conditions of constant temperature, is operationally the simpler. We point out that equation 163 will not give $U = \mu N$ on integration, because $\mu(N, \sigma, V)$ is a function of N.

Using equation 164 at constant volume $(dV = 0)$ and constant entropy $(d\sigma = 0)$, we obtain

$$0 = \frac{1}{\tau} dU - \frac{\mu}{\tau} dN \tag{166}$$

where I have replaced the partial derivative of entropy with respect to energy by inverse temperature and the partial derivative of entropy with respect to particle number by equation 165. From here equation 163 naturally follows. The full derivatives are replaced by partials because we have kept volume and entropy constant:

$$\mu = \left. \frac{\partial U}{\partial N} \right|_{\sigma,V} \quad \square \tag{167}$$

K&K 5.15

Consider a system at temperature τ, with N atoms of mass M in volume V. Let $\mu(0)$ denote the value of the chemical potential at the surface of the Earth.

Part a

Prove carefully and honestly that the value of the total chemical potential for the identical system when translated to altitude h is

$$\mu(h) = \mu(0) + Mgh \tag{168}$$

where g is the acceleration of gravity.

If we don't change the state of the system, moving it to a height h adds the potential energy Mgh for each particle, or a total energy of $MghN$. Thus, when we write down the partition function, all the terms will have the same exponential factor $exp(-MghN/\tau)$:

$$Z(h) = Z(0)exp(-MghN/\tau) \tag{169}$$

Therefore the free energy will be

$$F = -\tau ln(Z) = -\tau ln[Z(0)] + MghN = F(0) + MghN \tag{170}$$

leading to the chemical potential

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{\tau,V} = \mu(0) + Mgh \quad \square \tag{171}$$

Part b

Why is this result different from that applicable to the barometric equation of an isothermal atmosphere?

In the barometric problem, the chemical potential was independent of the height because the system at any height h was at diffusive equilibrium with the system at any other height h'. There is no a priori reason for these two systems to be in diffusive contact with each other unless we do something to them. Since we haven't brought them in diffusive contact, particles aren't flowing from the upper to the lower system (upper systems has higher chemical potential) until the chemical potentials are equal. The way the problem is set up, there is no diffusive contact, so we get a different result.

K&K 6.3

Distribution function for double occupancy statistics: Let us imagine a new mechanics in which the allowed occupancies of an orbital are 0, 1, and 2. The values of the energy associated with the occupancies are assumed to be 0, ϵ, and 2ϵ, respectively.

Part a

Derive an expression for the ensemble average occupancy $\langle N \rangle$, when the system composed of this orbital is in thermal and diffusive contact with a reservoir at temperature τ and chemical potential μ.

To begin we write down the Gibbs sum for this new mechanics:

$$\mathcal{Z} = 1 + exp((\mu - \epsilon)/\tau) + exp((2\mu - 2\epsilon)/\tau) \tag{172}$$

then the average occupation number is:

$$\langle N \rangle = \frac{exp((\mu - \epsilon)/\tau) + 2exp((2\mu - 2\epsilon)/\tau)}{1 + exp((\mu - \epsilon)/\tau) + exp((2\mu - 2\epsilon)/\tau)} \quad \square \tag{173}$$

Part b

Return now to the usual quantum mechanics, and derive an expression for the ensemble average occupancy of an energy level which is doubly degenerate; that is, two orbitals have the identical energy ϵ. If both orbitals are occupied the total energy is

2ϵ.

If two orbitals have the identical energy ϵ we must add a factor of 2 in front of that term in the Gibbs sum (remember that the equation for the Gibbs (and Boltzmann) sum has a factor for the degeneracy of a state. It is just rarely included since the states are usually non degenerate):

$$\mathcal{Z} = 1 + 2exp((\mu - \epsilon)/\tau) + exp((2\mu - 2\epsilon)/\tau) = [1 + exp((\mu - \epsilon))/\tau)]^2 \tag{174}$$

and similarly for the average occupancy:

$$\langle N \rangle = \frac{2exp((\mu - \epsilon)/\tau) + exp((2\mu - 2\epsilon)/\tau)}{[1 + exp((\mu - \epsilon))/\tau)]^2} = \frac{2}{exp((\epsilon - \mu)/\tau) + 1} \quad \square \tag{175}$$

The occupancy is just twice the Fermi-Dirac distribution.

K&K 6.4

Energy of a gas of extreme relativistic particles: Extreme relativistic particles have momenta p such that $pc \gg Mc^2$, where M is the rest mass of the particle. The de Broglie relation $\lambda = h/p$ for the quantum wavelength continues to apply. Show that the mean energy per particle of an extreme relativistic ideal gas is 3τ if $\epsilon \approx pc$, in contrast to $3\tau/2$ for the non relativistic problem.

The probability of a state with energy $E = pc$ is $\sim exp(-pc/\tau)$. So:

$$\langle E \rangle = \langle pc \rangle = \frac{\int d^3p \; pc \; exp(-pc/\tau)}{\int d^3p \; exp(-pc/\tau)} = \tau \frac{\int d^3x \; x \; exp(-x)}{\int d^3x \; exp(-x)} = \tau \frac{\int dx \; x^3 \; exp(-x)}{\int dx \; x^2 \; exp(-x)} \tag{176}$$

where we have made the substitution $x = pc/\tau$. These integrals (understood to go from 0 to ∞) are just gamma functions. The numerator is equal to $\Gamma(3) = 3!$ and the denominator is equal to $\Gamma(2) = 2!$ and therefore:

$$\langle E \rangle = 3\tau \quad \square \tag{177}$$

K&K 6.5

Integration of the thermodynamic identity for an ideal gas: From the thermodynamic identity at constant number of particles we have

$$d\sigma = \frac{dU}{\tau} + \frac{pdV}{\tau} = \frac{1}{\tau}\frac{\partial U}{\partial \tau}\bigg|_V d\tau + \frac{1}{\tau}\frac{\partial U}{\partial V}\bigg|_\tau dV + \frac{pdV}{\tau} \tag{178}$$

Show by integration that for an ideal gas the entropy is

$$\sigma = C_V ln(\tau) + N ln(V) + \sigma_1 \tag{179}$$

where σ_1 is a constant, independent of τ and V.

We start with the fact that for an ideal gas, $U = 3N\tau/2$. Plugging in the derivatives of this expression into equation 178 yields:

$$d\sigma = \frac{1}{\tau}\frac{3}{2}Nd\tau + \frac{pdV}{\tau} \tag{180}$$

Furthermore, for an ideal gas, $p/\tau = N/V$, and $\partial U/\partial \tau|_V \equiv C_V$, so the above becomes:

$$d\sigma = \frac{d\tau}{\tau}C_V + N\frac{dV}{V} \tag{181}$$

Integrating both sides yields the required result:

$$\sigma = C_V ln(\tau) + N ln(V) + \sigma_1 \quad \square \tag{182}$$

K&K 6.6

Entropy of mixing: Suppose that a system of N atoms of type A is placed in diffusive contact with a system of N atoms of type B at the same temperature and volume.

Show that after diffusive equilibrium is reached the total entropy is increased by $2N ln2$. This entropy increase is known as the entropy of mixing. If the atoms are identical $(A \equiv B)$, show that there is no increase in entropy when diffusive contact is established. The difference in the results has been called the Gibbs paradox.

The Sackur-Tetrode equation tells us the entropy of an ideal gas of N atoms with concentration $n = N/V$:

$$\sigma = N[ln\frac{n_Q}{n} + \frac{5}{2}] = N[lnV + \frac{3}{2}lnT + \sigma_1] \tag{183}$$

where σ_1 is a constant. Before the gases are put in diffusive contact, gases A and B have g_A and g_B states accessible to them, respectively, and thus after they come in diffusive contact the system has $g_A g_B \equiv g$ states accessible to it. Therefore, the entropy simply adds: $\sigma = \sigma_A + \sigma_B$. Initially, we have the entropy due to both gases (where $N_A = N_B$, $V_A = V_B$):

$$\sigma_{initial} = NlnV + \frac{3}{2}NlnT + N\sigma_1 + NlnV + \frac{3}{2}NlnT + N\sigma_1 = 2N[lnV + \frac{3}{2}lnT + \sigma_1] \tag{184}$$

After the gases mix, the temperature doesn't change, since they were originally at the same temperature, and no work was done. However, $V \to 2V$ and $N \to 2N$

$$\sigma_{final} = 2N[ln2V + \frac{3}{2}lnT + \sigma_1] \tag{185}$$

So the difference in entropy is

$$\sigma_{final} - \sigma_{initial} = 2Nln2V - 2NlnV = 2Nln2 \quad \square \tag{186}$$

K&K 6.10
Isentropic relations of ideal gas:
Part a
Show that the differential changes for an ideal gas in an isentropic process satisfy:

$$\frac{dp}{p} + \gamma\frac{dV}{V} = 0 \tag{187}$$

$$\frac{d\tau}{\tau} + (\gamma - 1)\frac{dV}{V} = 0 \tag{188}$$

$$\frac{dp}{p} + \frac{\gamma}{(1-\gamma)}\frac{d\tau}{\tau} = 0 \tag{189}$$

where $\gamma = C_p/C_V$; these relations apply even if the molecules have internal degrees of freedom.

We start with the first law of thermodynamics

$$d\sigma = \frac{dU}{\tau} + \frac{pdV}{\tau} = 0 \tag{190}$$

where the 0 corresponds to an isentropic process. Next, recall that for an ideal gas, $U = 3N\tau/2 = C_V\tau$, and $p/\tau = nR/V$ Plugging this in:

$$C_V\frac{d\tau}{\tau} + nR\frac{dV}{V} = 0 \tag{191}$$

Now recall the relation $C_p - C_V = nR$. Putting this into the above yields:

$$C_V\frac{d\tau}{\tau} + (C_p - C_V)\frac{dV}{V} = 0 \quad \Rightarrow \quad \frac{d\tau}{\tau} + (\gamma - 1)\frac{dV}{V} = 0 \quad \square \tag{192}$$

where I have divided by C_V.
On the other hand, I can replace τ by $pV/(C_p - C_V)$, leading to

$$d\tau = (Vdp + pdV)/(C_p - C_V) \tag{193}$$

Plugging this into equation 191 gives:

$$C_V \frac{(V\,dp + p\,dV)}{(C_p - C_V)}\frac{(C_p - C_V)}{pV} + (C_p - C_V)\frac{dV}{V} = 0 \tag{194}$$

Simplifying:

$$C_V \frac{dp}{p} + C_p \frac{dV}{V} = 0 \quad \Rightarrow \quad \frac{dp}{p} + \gamma\frac{dV}{V} = 0 \quad \square \tag{195}$$

where I have canceled some terms involving $C_V\,dV/V$.

To get the last relation, I need to get rid of V. By the ideal gas law, $V = (C_p - C_V)\tau/p$, meaning that

$$dV = (C_p - C_V)[\frac{d\tau}{p} - \frac{\tau\,dp}{p^2}] \tag{196}$$

Plugging this into the simplified isentropic form of the first law:

$$C_V \frac{d\tau}{\tau} + nR\frac{dV}{V} = 0 \quad \Rightarrow \quad C_V\frac{d\tau}{\tau} + (C_p - C_V)(\frac{d\tau}{\tau} - \frac{dp}{p}) = 0 \tag{197}$$

and canceling terms and simplifying leads to

$$C_p \frac{d\tau}{\tau} + (C_V - C_p)\frac{dp}{p} = 0 \quad \Rightarrow \quad \frac{dp}{p} + \frac{\gamma}{1-\gamma}\frac{d\tau}{\tau} \quad \square \tag{198}$$

Part b
The isentropic and isothermal bulk moduli are defined as

$$B_\sigma = -V\frac{\partial p}{\partial V}\Big|_\sigma ; \quad B_\tau = -V\frac{\partial p}{\partial V}\Big|_\tau \tag{199}$$

Show that for an ideal gas $B_\sigma = \gamma p$; $B_\tau = p$. The velocity of sound in a gas is given by $c = \sqrt{B_\sigma/\rho}$; there is very little heat transfer in a sound wave. For an ideal gas of molecules of mass M we have $p = \rho\tau/M$, so that $c = \sqrt{\gamma\tau/M}$. Here ρ is the mass density.
The first relation is simple. Using the relation 201, we can convert the full derivatives to partial derivatives, since the process is at constant entropy anyway.

$$\frac{dp}{p} = -\gamma\frac{dV}{V} \quad \Rightarrow \quad \frac{\partial p}{\partial V}\Big|_\sigma = -\gamma\frac{p}{V} \quad \Rightarrow \quad B_\sigma = \gamma p \quad \square \tag{200}$$

The second relation follows via a simple usage of the ideal gas law: $p = N\tau/V$, so at constant temperature, $\partial p/\partial V = -N\tau/V^2 = -p/V$. Therefore,

$$B_\tau = -V\frac{\partial p}{\partial V}\Big|_\tau = -V\frac{-p}{V} = p \quad \square \tag{201}$$

K&K 6.12
Ideal gas in two dimensions:
Part a
Find the chemical potential of an ideal monatomic gas in two dimensions, with N atoms confined to a square of area $A = L^2$. The spin is zero.
The partition function is

$$Z = \frac{1}{N!}\prod_N \int d^2r \frac{1}{h^2}\int_0^\infty d^2p\, exp(-p^2/2m\tau) = \frac{A^N}{N!h^{2N}}\{\int_0^\infty dp_x\,dp_y exp(-(p_x^2 + p_y^2)/2m\tau)\}^N \tag{202}$$

The integral over p_x will of course equal the integral over p_y, so we can simplify things by writing

$$Z = \frac{A^N}{N!h^{2N}}\{[\int_0^\infty dp\, exp(-p^2/2m\tau)]^2\}^N \tag{203}$$

We can make it a dimensionless quantity by introducing the variable $x = p^2/2m\tau$, meaning that $dp = dx\sqrt{\frac{m\tau}{x}}$. The integral then becomes

$$Z = \frac{A^N}{N!h^{2N}}\sqrt{2m\tau}^{2N}\{[\int_0^\infty dx\, x^{-1/2}\, exp(-x)]^2\}^N = \frac{A^N}{N!h^{2N}}\sqrt{2m\tau}^{2N}[\Gamma(\frac{1}{2})]^{2N} \tag{204}$$

and using the fact that $\Gamma(1/2) = \sqrt{\pi}$, we obtain that the partition function of an ideal gas in two dimensions is

$$Z_{2d} = \frac{A^N}{N!}\{\frac{2\pi m\tau}{h^2}\}^N \tag{205}$$

Compare this with the partition function of a gas in 3 dimensions

$$Z_{3d} = \frac{V^N}{N!}\{\frac{2\pi m\tau}{h^2}\}^{3N/2} \tag{206}$$

The only difference is that $3N/2 \to 2N/2$. Now that we have the ideal gas partition function, we can calculate the free energy

$$F = -\tau ln[\frac{A^N}{N!}\{\frac{2\pi m\tau}{h^2}\}^N] = -\tau[NlnA - NlnN + N + Nln(\frac{2\pi m\tau}{h^2})] \tag{207}$$

where I have used Stirling's approximation. I can now use the definition of the chemical potential:

$$\mu = \frac{\partial F}{\partial N}\Big|_{\tau,A} = -\tau lnA + \tau lnN - \tau ln(\frac{2\pi m\tau}{h^2}) \tag{208}$$

In particular, if I identify $n_2 = N/A$ as the two dimensional analog of $n = N/V$ and $n_{Q2} = 2\pi m\tau/h^2$ as the two dimensional analog of the three dimensional quantum concentration, I obtain that the chemical potential is

$$\mu = \tau ln[\frac{n_2}{n_{Q2}}] \quad \square \tag{209}$$

which is the same as the three-dimensional case.

Part b
Find an expression for the energy U of the gas.
I can do this in two ways. I can use the equipartition theorem to note that there are now two degrees of freedom, and that therefore the energy is $N\tau/2 + N\tau/2 = N\tau$. Or I can use the partition function in equation 205:

$$U = \tau^2\frac{\partial(lnZ)}{\partial\tau} = \tau^2\frac{\partial}{\partial\tau}ln[NlnA - NlnN + N + Nln(\frac{2\pi m\tau}{h^2})] = N\tau \quad \square \tag{210}$$

Unsurprisingly, I get the same answer both ways.

Part c
Find an expression for the entropy σ. The temperature is τ.
Using the definition of the free energy, $F = U - \tau\sigma$, we can get the entropy from $\sigma = (U - F)/\tau$.

$$\sigma = \frac{1}{\tau}(N\tau + \tau[NlnA - NlnN + N + Nln(\frac{2\pi m\tau}{h^2})]) = 2N + NlnA - NlnN + Nln(\frac{2\pi m\tau}{h^2}) \tag{211}$$

Once again, identifying the two dimensional concentration and quantum concentration as in part a, I can get that the entropy is

$$\sigma = 2N + Nln[\frac{n_{Q2}}{n_2}] \quad \square \tag{212}$$

K&K 6.14
Ideal gas calculations: Consider one mole of an ideal monatomic gas at $300\ K$ and 1 atm. First, let the gas expand isothermally and reversibly to twice the initial volume; second, let this be followed by an isentropic expansion from twice to four times the initial volume.

Part a

How much heat (in joules) is added to the gas in each of these two processes?

The first law of thermodynamics, $dU = dQ - pdV$ with $dU = 0$ yields for the isothermal expansion

$$dQ = \int_V^{2V} pdV = nR\tau \int_V^{2V} \frac{dV}{V} = nRk_BT ln2 = 1,729\ J \quad \square \tag{213}$$

and for the second process, $dQ = 0$, since the process is isentropic (or adiabatic).

Part b

What is the temperature at the end of the second process?

Just to be clear, the temperature doesn't change during the first, isothermal process. For the second process, we will use the result that $TV^{\gamma-1} = constant$ along an adiabat. If $V_1 = 2V_0$ is the volume after the isothermal expansion and $V_2 = 4V_0$ is the volume after the isentropic expansion then:

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \quad \Rightarrow \quad T_2 = T_1(\frac{V_1}{V_2})^{\gamma-1} \tag{214}$$

with $\gamma = 5/3$ for an ideal gas and $V_1/V_2 = 1/2$, we obtain that $T_2 = 300\ K \times (.25)^{2/3} = 189\ K$ $\quad \square$

Part c

Suppose the first process is replaced by an irreversible expansion into a vacuum, to a total volume twice the initial volume. What is the increase of entropy in the irreversible expansion, in joules per kelvin?

From the Sakur-Tetrode equation, $\sigma \propto Nk_B ln V$, so

$$\Delta\sigma = Nk_B ln(2V) - Nk_B ln V = Nk_B ln2 = 5.76\ JK^{-1} \quad \square \tag{215}$$

K&K 6.15

Diesel engine compression: A diesel engine is an internal combustion engine in which fuel is sprayed into the cylinders after the air charge has been so highly compressed that it has attained a temperature sufficient to ignite the fuel. Assume that the air in the cylinders is compressed isentropically from an initial temperature of 27°C (300 K). If the compression ratio is 15, what is the maximum temperature in °C to which the air is heated by the compression. Take $\gamma = 1.4$.

This is a simple problem masquerading behind a lot of words. Use the constancy of $TV^{\gamma-1}$ along an adiabat.

$$T_2 = T_1(\frac{V_1}{V_2})^{\gamma-1} = 300\ K \times 15^{1.4-1} = 886\ K = 613°C \quad \square \tag{216}$$

K&K 7.1

Density of orbitals in one and two dimensions:

Part a

Show that the density of orbitals of a free electron in one dimension is

$$\mathcal{D}_1(\epsilon) = \frac{L}{\pi}\sqrt{\frac{2m}{\hbar^2\epsilon}} \tag{217}$$

where L is the length of the line.

In one dimension, $\psi(x) = sin(n\pi x/L)$. Whereas in the three dimensional case the number of electrons up to some energy level n is given by the volume of the octant of the spherical shell of radius n, in one dimension there is no sphere and it is simply a line of length n. We still need to account for the electron spin, so the total number of electrons up to level n is $N = 2n$. We plug this into the energy of the electrons:

$$\epsilon = \frac{\pi^2\hbar^2}{2mL^2}n^2 \quad \Rightarrow \quad \epsilon = \frac{\pi^2\hbar^2}{8mL^2}N^2 \quad \Rightarrow \quad N = \frac{L}{\pi\hbar}\sqrt{8m\epsilon} \tag{218}$$

Now we recall that the density of orbitals is $dN/d\epsilon$.

$$\mathcal{D}_1(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{L}{\pi\hbar}\sqrt{\frac{2m}{\epsilon}} \quad \square \tag{219}$$

Part b
Show that in two dimensions, for a square of area A,

$$\mathcal{D}_2(\epsilon) = \frac{Am}{\pi \hbar^2} \tag{220}$$

independent of ϵ.

The total number of electrons up to the energy level n is given by the area of the circle of side n (remembering to account for the 2 due to the electron spin and the 1/4 because we only want the positive values of n): $N = 2 \times \frac{1}{4} \times \pi n^2$. Therefore, in terms of N, the particle in a box energies are:

$$\epsilon = \frac{\pi \hbar^2}{mL^2} N \quad \Rightarrow \quad N = \frac{mL^2}{\pi \hbar^2} \epsilon \tag{221}$$

which means that the density of states $dN/d\epsilon$ is

$$\mathcal{D}_2(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{Am}{\pi \hbar^2} \quad \square \tag{222}$$

where I have replaced L^2 with the area A.

K&K 7.2
Energy of relativistic Fermi gas: For electrons with an energy $\epsilon \gg mc^2$, where m is the rest mass of the electron, the energy is given by $\epsilon = pc$, where p is the momentum. For electrons in a cube of volume $V = L^3$ the momentum is of the form $\hbar \pi / L$ multiplied by $(n_x^2 + n_y^2 + n_z^2)^{1/2}$, exactly as for the non relativistic limit.

Part a
Show that in this extreme relativistic limit the Fermi energy of a gas of N electrons is given by

$$\epsilon_F = \hbar \pi c \left(\frac{3n}{\pi} \right)^{1/3} \tag{223}$$

where $n = N/V$.

We still want to replace the quantum number of the energy level, n, by the number of particles in the gas, N. To do this, we write down the number of particles up to the nth energy level, just like in the non relativistic case:

$$N = 2 \times \frac{1}{8} \times \frac{4\pi}{3} n_F^3 \quad \Rightarrow \quad n_F = \left(\frac{3N}{\pi} \right)^{1/3} \tag{224}$$

meaning that the momentum is

$$p = \frac{\hbar \pi}{L} n_F = \frac{\hbar \pi}{L} \left(\frac{3N}{\pi} \right)^{1/3} = \hbar \pi \left(\frac{3N}{V\pi} \right)^{1/3} \tag{225}$$

where I have replaced L by $V^{1/3}$. Therefore the Fermi energy is $\epsilon = pc$:

$$\epsilon = c\hbar \pi \left(\frac{3N}{V\pi} \right)^{1/3} = c\hbar \pi \left(\frac{3n}{\pi} \right)^{1/3} \quad \square \tag{226}$$

with n now the particle density N/V.

Part b
Show that the total energy of the ground state of the gas is

$$U_0 = \frac{3}{4} N \epsilon_F \tag{227}$$

We want to calculate

$$U_{ground} = \sum_n \epsilon(n) \rightarrow \pi \int_0^{n_F} n^2 \epsilon(n) dn = \frac{3N}{4} \epsilon_F \quad \square \tag{228}$$

K&K 7.3

Pressure and entropy of a degenerate Fermi gas:

Part a

Show that a Fermi electron gas exerts a pressure

$$p = \frac{(3\pi^2)^{2/3}}{5} \frac{\hbar^2}{m} \left(\frac{N}{V}\right)^{5/3} \tag{229}$$

We need to calculate $p = -\partial U/\partial V|_{\sigma,N}$. Now, since the system is in the ground state, a change of volume is a change of constant entropy, so we can safely neglect the constant entropy in the partial derivatives.

$$p = -\frac{\partial U_0}{\partial V}\Big|_N = -\frac{\partial}{\partial V}\frac{3}{5}N\epsilon_F = -\frac{\partial}{\partial V}\frac{3}{5}N\frac{\hbar^2}{2m}(3\pi^2 N)^{2/3}V^{-2/3} \tag{230}$$

From which we easily obtain

$$p = \frac{(3\pi^2)^{2/3}}{5} \frac{\hbar^2}{m} \left(\frac{N}{V}\right)^{5/3} \quad \Box \tag{231}$$

Part b

In a uniform decrease of the volume of a cube every orbital has its energy raised: The energy of an orbital is proportional to $1/L^2$ or to $1/V^{2/3}$. Find an expression for the entropy of a Fermi electron gas in the region $\tau \ll \epsilon_F$. Notice that $\sigma \to 0$ as $\tau \to 0$.

We use the relation

$$C_V = \tau \frac{\partial \sigma}{\partial \tau}\Big|_V \tag{232}$$

According to equation 7.37 in Kittel and Kroemer, the heat capacity of a Fermi gas is

$$C_V = \frac{dU}{d\tau} = \int_0^\infty d\epsilon (\epsilon - \epsilon_F)\frac{df}{d\tau}\mathcal{D}(\epsilon) = \frac{\pi^2 N\tau}{2\epsilon_F} \tag{233}$$

since the heat capacity is proportional to τ, the entropy can simply be integrated from the above heat capacity and is in fact equal to the heat capacity:

$$\sigma = \frac{\pi^2 N\tau}{2\epsilon_F} \quad \Box \tag{234}$$

K&K 7.6

Mass-Radius Relationship for White Dwarfs: Consider a white dwarf of mass M and radius R. Let the electrons be degenerate but non relativistic; the protons are non degenerate.

Part a

Show that the order of magnitude of the gravitation self-energy is $-GM^2/R$, where G is the gravitational constant. (If the mass density is constant within the sphere of radius R, the exact potential energy is $-3GM^2/5R$.

The self-energy has units of $erg = dyne \cdot cm$. Furthermore, by convention it is negative. The correct combination of the mass, radius, and gravitational constant is (and hopefully you remember this equation from introductory physics):

$$U_{g.s.e.} = -\frac{GM_{WD}^2}{R_{WD}} \quad \Box \tag{235}$$

Part b

Show that the order of magnitude of the kinetic energy of the electrons in the ground state is

$$\frac{\hbar^2 N^{5/3}}{mR^2} \approx \frac{\hbar^2 M^{5/3}}{mM_H^{5/3}R^2} \tag{236}$$

where m is the mass of an electron and M_H is the mass of a proton.

The kinetic energy of a fermi gas of electrons is $U_0 = 3N\epsilon_F/5$. Plugging in the equation for the Fermi energy:

$$U_0 = \frac{3N\epsilon_F}{5} = \frac{3N}{5}\frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \propto \frac{\hbar^2 N^{5/3}}{mR^2} \quad \square \tag{237}$$

where I have replaced $V^{2/3}$ with R^2. To get the second equality, note that the number of electrons is equal to the number of hydrogen atoms which is equal to the ratio of the mass of the star to the mass of hydrogen. Therefore:

$$U_0 = \frac{\hbar^2 N^{5/3}}{mR^2} \propto \frac{\hbar^2 M^{5/3}}{mM_H^{5/3}R^2} \quad \square \tag{238}$$

Part c

Show that the gravitational and kinetic energies are of the same order of magnitude (as required by the virial theorem of mechanics), $M^{1/3}R \approx 10^{20}g^{1/3}cm$.

We set the gravitational and kinetic energies equal to each other

$$-\frac{GM^{6/3}}{R} = \frac{\hbar^2 M^{5/3}}{mM_H^{5/3}R^2} \quad \Rightarrow \quad M^{1/3}R = -\frac{\hbar^2}{GmM_H^{5/3}} \quad \square \tag{239}$$

K&K 7.14

Two Orbital Boson System: Consider a system of N bosons of spin zero, with orbitals at the single particle energies 0 and ϵ. The chemical potential is μ, and the temperature is τ. Find τ such that the thermal average population of the lowest orbital is twice the population of the orbital at ϵ. Assume $N \gg 1$ and make what approximations are reasonable.

The Bose-Einstein distribution function is

$$f_{BE}(\epsilon, \tau) = \frac{1}{exp((\epsilon_i - \mu)/\tau) - 1} \tag{240}$$

So the occupation of the ground level ($\epsilon = 0$) is

$$f_{BE}(0) = \frac{1}{exp(-\mu/\tau) - 1} \tag{241}$$

and the occupation number of the first excited state

$$f_{BE}(1) = \frac{1}{exp((\epsilon - \mu)/\tau) - 1} \tag{242}$$

So we set twice the occupation of the first excited state equal to the ground state:

$$\frac{1}{exp(-\mu/\tau) - 1} = \frac{2}{exp((\epsilon - \mu)/\tau) - 1} \tag{243}$$

However, it is easier to solve this equation if we note that $2/3$ of the total number of particles are in the ground state and $1/3$ are in the first excited state.

$$\frac{1}{exp(-\mu/\tau) - 1} = \frac{2}{3}N \quad \Rightarrow \quad exp(-\mu/\tau) = \frac{3}{2N} + 1 \tag{244}$$

and

$$\frac{1}{exp((\epsilon - \mu)/\tau) - 1} = \frac{1}{3}N \quad \Rightarrow \quad exp((\epsilon - \mu)/\tau) = \frac{3}{N} + 1 \tag{245}$$

So dividing the above two equations by each other we get

$$exp(\epsilon/\tau) = 1 + \frac{3}{2N} \quad \Rightarrow \quad \tau \approx \frac{2N}{3}\epsilon \quad \square \tag{246}$$

where I have used the Taylor expansion of the logarithm. The important thing about the answer is that since the temperature where the majority of the particles is in the ground state is proportional to and of the order of the number of particles, Bose-Einstein condensates occur at temperatures *much* larger than the energy separation between the lowest and next-lowest orbitals.

K&K 8.1

Heat Pump:

Part a

Show that for a reversible heat pump the energy required per unit of heat delivered inside the building is given by the Carnot efficiency

$$\frac{W}{Q_h} = \eta_C = \frac{\tau_h - \tau_l}{\tau_h} \tag{247}$$

What happens if the heat pump is not reversible?

A reversible heat pump is just a Carnot engine. For any reversible process, the entropy generated in the heat pump must leave at the higher temperature τ_h, as in a refrigerator. Therefore, $\sigma_h = \sigma_l \Rightarrow Q_h/\tau_h = Q_l/\tau_l$, and the definition of the work is

$$W = Q_h - Q_l = Q_h - \frac{\tau_l}{\tau_h}Q_h \quad \Rightarrow \quad \frac{W}{Q_h} = \frac{\tau_h - \tau_l}{\tau_h} \equiv \eta_C \quad \square \tag{248}$$

If the heat pump were not reversible, some entropy would remain in the process which would require more work. The efficiency would be lower than the Carnot efficiency.

Part b

Assume that the electricity consumed by a reversible heat pump must itself be generated by a Carnot engine operating between the temperatures τ_{hh} and τ_l. What is the ratio Q_{hh}/Q_h of the heat consumed at τ_{hh} to the heat delivered at τ_h?

If the electricity is generated by a Carnot engine than the work done by that Carnot engine is

$$W = Q_{hh} - \frac{\tau_l}{\tau_{hh}}Q_{hh} \tag{249}$$

Plugging this into equation 248 above gives

$$\frac{Q_{hh} - \frac{\tau_l}{\tau_{hh}}Q_{hh}}{Q_h} = \frac{\tau_h - \tau_l}{\tau_h} \tag{250}$$

which can be simplified to

$$\frac{Q_{hh}}{Q_h} = \frac{\tau_{hh}}{\tau_{hh} - \tau_l}\frac{\tau_h - \tau_l}{\tau_h} \quad \square \tag{251}$$

K&K 8.3

Photon Carnot Enginer: Consider a Carnot engine that uses as the working substance a photon gas.

Part a

Given τ_h and τ_l as well as V_1 and V_2 determine V_3 and V_4.

The entropy of a photon gas goes as $\sigma \propto V\tau^3$ (see equation 4.23 in K&K). The energy goes as $U \propto V\tau^4$ (4.20 in K&K). Therefore, for an adiabatic process, $V\tau^3$ is constant, while in an isothermal process, $V\tau^4$ is constant. V_1 is related to V_4 via

$$V_1\tau_l^3 = V_4\tau_h^3 \quad \Rightarrow \quad V_4 = \frac{\tau_l^3}{\tau_h^3}V_1 \quad \square \tag{252}$$

while the relation between V_2 and V_3 is

$$V_2\tau_l^3 = V_3\tau_h^3 \quad \Rightarrow \quad V_3 = \frac{\tau_l^3}{\tau_h^3}V_2 \quad \square \tag{253}$$

since there is an adiabatic path between volumes V_1 and V_4 and between V_2 and V_3.

Part b

What is the heat Q_h taken up and the work done by the gas during the first isothermal expansion? Are they equal to each other, as for the ideal gas?

Using the first law of thermodynamics:

$$Q_h = \tau_h \int_1^2 d\sigma = \tau_h(\sigma_2 - \sigma_1) = \frac{4}{3}s\tau_h^4(V_2 - V_1) \quad \square \tag{254}$$

which equals the work.

Part c

Do the two isentropic stages cancel each other, as for the ideal gas?

No because they operate at different volumes. **Part d**

Calculate the total work done by the gas during one cycle. Compare it with the heat taken up at τ_h and show that the energy conversion efficiency is the Carnot efficiency.

$$W = -(W_{12} + W_{23} + W_{34} + W_{41}) \tag{255}$$

and we know that

$$W_{12} + W_{34} = -\frac{s\tau_h^3}{3}(\tau_h - \tau_l)(V_2 - V_1) \tag{256}$$

while

$$W_{23} + W_{41} = -\sigma\tau_h^3(\tau_h - \tau_l)(V_2 - V_1) \tag{257}$$

Therefore, dividing by the heat in equation 254

$$\frac{W}{Q_h} = \frac{\tau_h - \tau_l}{\tau_h} = \eta_C \quad \square \tag{258}$$

K&K 8.7

Light Bulb in the Refrigerator: A 100W light bulb is left burning inside a Carnot refrigerator that draws 100W. Can the refrigerator cool below room temperature?

Yes because the work and the heat are the same, so $T_h - T_l = T_l$ or $T_l = T_h/2 \approx 150K$.

K&K 8.10

Irreversible Expansion of a Fermi Gas: Consider a gas of N noninteracting spin $1/2$ fermions of mass M, initially in a volume V_i at temperature $\tau_l = 0$. Let the volume gas expand irreversibly into a vacuum, without doing work, to a final volume V_f. What is the temperature of the gas after expansion if V_f is sufficiently large for the classical limit to apply? Estimate the factor by which the gas should be expanded for its temperature to settle to a constant final value.

A Fermi gas has average energy per particle

$$\langle \epsilon \rangle = \frac{3}{5}\epsilon_F = \frac{3\hbar^2}{10m}(3\pi^2\frac{N}{V_i})^{2/3} \tag{259}$$

After the expansion to volume V_f, the classical limit applies, where the average energy per particle is $\langle \epsilon \rangle = 3\tau/2$. We can equate the two energies to find that

$$\tau = \frac{2}{5}\epsilon_F = \frac{2\hbar^2}{10m}(3\pi^2\frac{N}{V_i})^{2/3} \quad \square \tag{260}$$

The classical limit applies if the concentration N/V_f is much less than the quantum concentration so

$$\frac{N}{V_f} \ll n_Q = (\frac{m\tau}{2\pi\hbar^2})^{3/2} \quad \Rightarrow \quad \frac{N}{V_f} \ll \frac{3}{5}\sqrt{\frac{\pi}{10}}\frac{N}{V_i} \tag{261}$$

Therefore:

$$\frac{V_f}{V_i} \gg \frac{5}{3}\sqrt{\frac{10}{\pi}} \approx 3 \quad \square \tag{262}$$

K&K 9.1
Thermal Expansion Near Absolute Zero:
Part a
Prove the three Maxwell relations:

$$\left.\frac{\partial V}{\partial \tau}\right|_p = -\left.\frac{\partial \sigma}{\partial p}\right|_\tau \tag{263}$$

$$\left.\frac{\partial V}{\partial N}\right|_p = \left.\frac{\partial \mu}{\partial p}\right|_N \tag{264}$$

$$\left.\frac{\partial \mu}{\partial \tau}\right|_N = -\left.\frac{\partial \sigma}{\partial N}\right|_\tau \tag{265}$$

Strictly speaking, equation 263 should be written

$$\left.\frac{\partial V}{\partial \tau}\right|_{p,N} = -\left.\frac{\partial \sigma}{\partial p}\right|_{\tau,N} \tag{266}$$

and two subscripts should appear similarly in equations 264 and 265. It is common to omit those subscripts that occur on both sides of the equalities.
We'll start with the Gibbs function:

$$G = U - \tau\sigma + pV \quad \Rightarrow \quad dG = dU - \sigma d\tau - \tau d\sigma + pdV + Vdp \tag{267}$$

But since $\tau d\sigma = dU - \mu dN + pdV$, we get

$$dG = \mu dN - \sigma d\tau + Vdp \tag{268}$$

Therefore, taking derivatives:

$$\left.\frac{\partial G}{\partial \tau}\right|_{p,N} = -\sigma, \quad \left.\frac{\partial G}{\partial N}\right|_{\tau,p} = \mu, \quad \left.\frac{\partial G}{\partial p}\right|_{\tau,N} = V \tag{269}$$

We can then take cross derivatives:

$$\frac{\partial^2 G}{\partial N \partial \tau} = -\left.\frac{\partial \sigma}{\partial N}\right|_\tau, \quad \frac{\partial^2 G}{\partial \tau \partial N} = \left.\frac{\partial \mu}{\partial \tau}\right|_N \tag{270}$$

$$\frac{\partial^2 G}{\partial \tau \partial p} = \left.\frac{\partial V}{\partial \tau}\right|_p, \quad \frac{\partial^2 G}{\partial p \partial \tau} = -\left.\frac{\partial \sigma}{\partial p}\right|_\tau \tag{271}$$

$$\frac{\partial^2 G}{\partial N \partial p} = \left.\frac{\partial V}{\partial N}\right|_p, \quad \frac{\partial^2 G}{\partial p \partial N} = \left.\frac{\partial \mu}{\partial p}\right|_N \tag{272}$$

Since the mixed partials are equal to each other, we get the Maxwell relations:

$$\left.\frac{\partial V}{\partial \tau}\right|_p = -\left.\frac{\partial \sigma}{\partial p}\right|_\tau, \quad \left.\frac{\partial \mu}{\partial \tau}\right|_N = -\left.\frac{\partial \sigma}{\partial N}\right|_\tau, \quad \left.\frac{\partial V}{\partial N}\right|_p = \left.\frac{\partial \mu}{\partial p}\right|_N \quad \square \tag{273}$$

Part b
Show with the help of equation 263 and the third law of thermodynamics that the volume coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial \tau}\right|_p \tag{274}$$

approaches zero as $\tau \to 0$.
We can rewrite the volume coefficient of thermal expansion (using the Maxwell relation) as:

$$\alpha = -\frac{1}{V}\left.\frac{\partial \sigma}{\partial p}\right|_\tau \tag{275}$$

However, recall that at low temperatures, the entropy becomes independent of the pressure, so the partial derivative of entropy with pressure is 0, making the coefficient of thermal expansion 0 at low temperatures as well. $\square$

K&K 10.1

Entropy, Energy and Enthalpy of a Van Der Waals Gas

Part a

Show that the entropy of the van der Waals gas is

$$\sigma = N\{ln[n_Q(V - Nb)/N + \frac{5}{2}]\} \tag{276}$$

Recall that for the ideal gas, the entropy is the Sackur-Tetrode equation $\sigma = N(ln(n_Q/n) + 5/2)$ (derived from the partition function of the ideal gas, then $F = -\tau lnZ$ and then $\sigma = \partial F/\partial \tau$). However, for the van der Waals gas, we will replace the ideal gas concentration $n = N/V$ with the van der Waals correction term $V \to V - Nb$, which accounts for the size of the molecules. Thus,

$$\sigma = N\{ln[n_Q(V - Nb)/N + \frac{5}{2}]\} \quad \square \tag{277}$$

Part b

Show that the energy is

$$U = \frac{3}{2}N\tau - \frac{N^2a}{V} \tag{278}$$

We use $F = U - \tau\sigma \Rightarrow U = F + \tau\sigma$. Now, F is the same as for the ideal gas, but this time we replace the volume with $V - Nb$ to account for the radius of the particles. The free energy of the van der Waals gas is in equation 10.38, so the energy is

$$U = \frac{3}{2}N\tau - \frac{N^2a}{V} \quad \square \tag{279}$$

Part c

Show that the enthalpy $H \equiv U + pV$ is

$$H(\tau, V) = \frac{5}{2}N\tau + \frac{N^2b\tau}{V} - \frac{2N^2a}{V} \tag{280}$$

$$H(\tau, p) = \frac{5}{2}N\tau + Nbp - 2Nap\tau \tag{281}$$

All results are given to first order in the van der Waals correction terms a,b.

Plugging in the equation of the van der Waals gas for $pV = N\tau/(1 - Nb/V) - N^2a/V$ and Taylor approximating it to $pV \approx N\tau(1 + Nb/V) - N^2a/V$, we obtain, using equation 279

$$H = \frac{5}{2}N\tau + \frac{N^2b\tau}{V} - \frac{2N^2a}{V} \tag{282}$$

To obtain equation 281, we insert the ideal gas relation $\tau/V = p/N$ into equation 282. Yes, it doesn't apply to the van der Waals gas, but it is a first order approximation.

$$H(\tau, p) = \frac{5}{2}N\tau + Nbp - 2Nap\tau \quad \square \tag{283}$$