Problem 1

Kittel & Kroemer, Chapter 6, problem 1 [Derivative of Fermi-Dirac function.]: 2 points

Show that $-\partial f / \partial \epsilon$ evaluated at the Fermi level $\epsilon = \mu$ has the value $(4\tau)^{-1}$. Thus the lower the temperature, thesteeper the slope of the Fermi-Dirac function.

Let's check:

$$\frac{\partial f}{\partial \epsilon} = \frac{\partial}{\partial \epsilon} \frac{1}{e^{(\epsilon-\mu)/\tau} + 1}$$

$$= -\frac{1}{\tau} \frac{e^{(\epsilon-\mu)/\tau}}{(e^{(\epsilon-\mu)/\tau} + 1)^2}.$$

Evaluating this at $\epsilon = \mu$ means $e^{(\epsilon-\mu)/\tau}$, so that $-\partial f / \partial \epsilon$ evaluated at $\epsilon = \mu$ gives $1/(4\tau)$.

Problem 2

Kittel & Kroemer, Chapter 6, problem 2 [Symmetry of filled and vacant orbitals.]: 2 points

Let $\epsilon = \mu + \delta$, so that $f(\epsilon)$ appears as $f(\mu + \delta)$. Show that

$$f(\mu + \delta) = 1 - f(\mu - \delta).$$

Thus the probability that an orbital δ above the Fermi level is occupied is equal to the probability an orbital δ below the Fermi level is vacant. A vacant orbital is sometimes known as a **hole**.

With this variable,

$$f(\mu + \delta) = \frac{1}{e^{\delta/\tau} + 1}$$

$$f(\mu - \delta) = \frac{1}{e^{-\delta/\tau} + 1}.$$

We can add them to see that

$$f(\mu + \delta) + f(\mu - \delta) = \frac{1}{e^{\delta/\tau} + 1} + \frac{1}{e^{-\delta/\tau} + 1}$$

$$= \frac{e^{-\delta/(2\tau)}}{e^{\delta/2\tau} + e^{-\delta/(2\tau)}} + \frac{e^{\delta/(2\tau)}}{e^{\delta/2\tau} + e^{-\delta/(2\tau)}}$$

$$= \frac{e^{\delta/2\tau} + e^{-\delta/(2\tau)}}{e^{\delta/2\tau} + e^{-\delta/(2\tau)}}$$

$$= 1,$$

Thus

$$f(\mu + \delta) = 1 - f(\mu - \delta).$$

Problem 3

Kittel & Kroemer, Chapter 6, problem 4 [Energy of gas of extreme relativistic particles.]: 3 points

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 $\epsilon \sim pc$, in contrast to $\frac{3}{2}\tau$ for the nonrelativistic problem.

We should re-evaluate the partition function for a single relativistic particle:

$$Z_1 = \sum_s e^{-\epsilon_s/\tau}.$$

The non-relativistic particle has kinetic energies $\frac{\hbar^2 \pi^2 (n_x^2 + n_y^2 + n_z^2)}{2ML^2}$, which should also be equal to $p^2/2M = (p_x^2 + p_y^2 + p_z^2)/2M$. By comparison, we can see that the momentum of the particle is given by $p_n = \pi\hbar\sqrt{n_x^2 + n_y^2 + n_z^2}/L$ (this can also be seen by acting the momentum operators $p_x = i\hbar\frac{\partial}{\partial x}$ on the wavefunction). So, if the energy in the relativistic case is $\epsilon \sim pc$, we have

$$Z_1 = \sum_{n_x, n_y, n_z = 1}^{\infty} e^{-\pi\hbar c\sqrt{n_x^2 + n_y^2 + n_z^2}/L\tau}.$$

In reality we shouldn't be starting the sum at $n_x, n_y, n_z = 1$, but only starting it for the lowest "extreme relativistic" particles. It turns out not to matter much if we are only interested in the limiting behavior, so we'll keep it as is. We can approximate this sum as an integral:

$$Z_1 = \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z e^{-\pi\hbar c\sqrt{n_x^2 + n_y^2 + n_z^2}/L\tau}.$$

We can change to spherical coordinates with $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$:

$$Z_1 = \frac{1}{8}4\pi \int_0^{\infty} dn\, n^2 e^{-\pi\hbar cn/L\tau}.$$

Changing variables to $x = \pi\hbar cn/L\tau$, we get

$$Z_1 = \frac{L^3\tau^3}{2\pi^2\hbar^2 c^3} \int_0^{\infty} dx\, x^2 e^{-x}.$$

Here the integral is just some number; it turns out to be equal to 2. Thus

$$Z_1 = \frac{L^3\tau^3}{\pi^2\hbar^2 c^3}.$$

The average energy of this particle is then

$$U_1 = \tau^2 \frac{\partial \ln Z_1}{\partial \tau} = \tau^2 \frac{\partial \ln(\tau^3)}{\partial \tau} = 3\tau.$$

Problem 4

Kittel & Kroemer, Chapter 6, problem 9 [Gas of atoms with internal degree of freedom.]

Consider an ideal monatomic gas, but one for which the atom has two internal energy states, one an energy Δ above the other. There are N atoms in volume V at temperature τ. Find the...

(a): 1 point

...chemical potential.

The comment on pp.162-163 of the textbook outlines how the chemical potential changes with various modifications to the ideal gas. In particular, it mentions that the chemical potential gets an additional term $-\tau \ln Z_{\text{int}}$ when there are internal degrees of freedom. If there are just two energy states, let's say with energies 0 and Δ, we can evaluate the internal partition function:

$$Z_{\text{int}} = e^0 + e^{-\Delta/\tau} = 1 + e^{-\Delta/\tau}.$$

(a): 1 point

Thus

$$\mu = \tau \ln(n/n_Q) - \tau \ln(1 + e^{-\Delta/\tau}).$$

(b): 1 point

...free energy.

We can now follow the book's procedure for the rest of the quantities:

$$F = \int_0^N \mu \, dN = \tau \int_0^N [\ln(n/n_Q) - \ln(1 + e^{-\Delta/\tau})]$$

$$= \tau \int_0^N [\ln(N) - \ln(n_Q V) - \ln(1 + e^{-\Delta/\tau})]$$

$$= N\tau[\ln(n/n_Q) - 1 - \ln(1 + e^{-\Delta/\tau})].$$

(b): 1 point

(c): 1 point

...entropy.

$$\sigma = -(\partial F/\partial \tau)_{V,N} = -N[\ln(n/n_Q) - 1 - \ln(1 + e^{-\Delta/\tau})] - N\tau[-\frac{3}{2\tau} - \frac{(\Delta/\tau^2)e^{-\Delta/\tau}}{1 + e^{-\Delta/\tau}}]$$

$$= -N[\ln(n/n_Q) - 1 - \ln(1 + e^{-\Delta/\tau})] + \frac{3N}{2} + \frac{N(\Delta/\tau)}{e^{\Delta/\tau} + 1}]$$

(c): 1 point

(d): 1 point

...pressure.

$$p = -(\partial F/\partial V)_{\tau,N} = N\tau/V.$$

(d): 1 point

(e): 1 point

...heat capacity at constant pressure.

The relationship $C_p = C_V + N$ still holds, so

$$C_p = (\partial U/\partial \tau)_p + N$$
$$= (\partial (F + \tau\sigma)/\partial \tau)_p + N.$$

We can see from above that $F + \tau\sigma = \frac{3}{2}N\tau + N\frac{\Delta/\tau}{e^{\Delta/\tau}+1}$; the energy is still just a function of the temperature, rather than the pressure and volume separately. Thus

(e): 1 point

$$C_p = (\partial(\frac{3}{2}N\tau + N\frac{\Delta/\tau}{e^{\Delta/\tau}+1})/\partial\tau)_p + N$$
$$= \frac{5}{2}N - N\frac{\Delta/\tau^2}{e^{\Delta/\tau}+1} + N\frac{(\Delta^2/\tau^3)e^{\Delta/\tau}}{(e^{\Delta/\tau}+1)^2}$$

Problem 5

Kittel & Kroemer, Chapter 6, problem 12 [Ideal gas in two dimensions.]

(a): 1 point

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 temperature is τ.

Let's compute:

$$Z_1 = \sum_{n_x, n_y} e^{-\hbar^2 \pi^2 (n_x^2 + n_y^2)/2ML^2\tau}$$

$$= \frac{1}{4} 2\pi \int_0^\infty dn\, n e^{-\hbar^2 \pi^2 n^2/2ML^2\tau}$$

$$= \frac{ML^2\tau}{\hbar^2\pi} \int_0^\infty dx\, x e^{-x^2}$$

$$= \frac{ML^2\tau}{2\pi\hbar^2}.$$

If there are N particles in the box, and we are in the classical regime where $f(\epsilon) = e^{(\mu-\epsilon)/\tau}$, then we have the constraint

$$N = \sum_s f(\epsilon_s)$$

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

$$= e^{\mu/\tau} Z_1.$$

We can solve this for the chemical potential:

$$\mu = \tau \ln(N/Z_1)$$

$$= \tau \ln \frac{2\pi\hbar^2 N}{ML^2\tau}.$$

(b): 1 point

Find an expression for the energy U of the gas.

The energy should be given by

$$U = \sum_s \epsilon_s f(\epsilon_s)$$

$$= \sum_s \epsilon_s e^{\beta(\mu-\epsilon_s)}$$

$$= e^{\beta\mu} \sum_s \epsilon_s e^{-\beta\epsilon_s}$$

$$= -e^{\beta\mu} \frac{\partial}{\partial\beta} \sum_s e^{-\beta\epsilon_s}$$

$$= -e^{\mu/\tau} \frac{\partial Z_1}{\partial\beta}.$$

We can use our result from part (a) for Z_1 and μ:

$$U = -e^{\ln \frac{2\pi\hbar^2 N}{ML^2\tau}} \frac{\partial}{\partial\beta} \frac{ML^2}{2\pi\hbar^2\beta}$$

$$= \frac{2\pi\hbar^2 N}{ML^2\tau} \frac{ML^2}{2\pi\hbar^2\beta^2}$$

$$= N\tau.$$

(b): 1 point

This is what we would expect from the classical equipartition theorem, since there are only two degrees of freedom in two dimensions. Note: this is not the only way to calculate U! You can calculate F and σ (like in the next part below) and then us $U = F + \tau\sigma$. Either way is fine.

(c): 1 point

Find an expression for the entropy σ.

We will start with the free energy using $(\partial F/\partial N)_{\tau,V} = \mu$ to find

$$F = \int_0^N \mu dN = \int_0^N \tau \ln \frac{2\pi\hbar^2 N}{ML^2\tau} dN$$

$$= \int_0^N \tau[\ln N + \ln \frac{2\pi\hbar^2}{ML^2\tau}] dN$$

$$= \tau[N\ln N - N + N\ln \frac{2\pi\hbar^2}{ML^2\tau}]$$

$$= \tau N \ln \frac{2\pi\hbar^2 N}{ML^2\tau} - \tau N.$$

(c): 1 point

Then

$$\sigma = (\partial F/\partial\tau)_{N,V} = N \ln \frac{2\pi\hbar^2 N}{ML^2\tau} - N + \tau N \frac{\partial}{\partial\tau} \ln \frac{2\pi\hbar^2 N}{ML^2\tau}$$

$$= N \left[\ln \frac{2\pi\hbar^2 N}{ML^2\tau} - 2 \right].$$

Problem 6

Kittel & Kroemer, Chapter 6, problem 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.

(a): 1 point

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

For a reversible, isothermal process, $Q = T\Delta S$. We showed in lecture that for an isothermal process, $\Delta S = nR\ln(V_2/V_1)$, where n is the number of moles and $R = 8.314$ J/mol K is the gas constant (recall that $Nk_B \equiv nR$. For the first step of our process then, $Q_1 = (300 \text{ K})R\ln(2) = 1730$ J.

x During an isentropic expansion, no heat is exchanged with the environment, so $Q_2 = 0$.

(a): 1 point

(b): 1 point

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

The temperature doesn't change during the first process, so the second process starts at $T = 300$ K. For an adiabatic transformation, we know $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$, where $\gamma = C_p/C_V$. For a monatomic ideal gas, $C_p = 5N/2$ and $C_V = 3N/2$ so that $\gamma = 5/3$. So we can calculate:

$$\begin{aligned} T_2 &= T_1(V_1/V_2)^{2/3} \\ &= (300 \text{ K})(1/2)^{2/3} \\ &= 189 \text{ K}. \end{aligned}$$

(b): 1 point

(c): 1 point

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?

In the irreversible expansion to twice the initial volume, each particle has increased its available number of states by a factor of 2. Since entropy is the logarithm of the number of available states, we expect that the entropy has increased by a factor of $\ln(2)$ per particle. Thus

$$\Delta S = R\ln 2 = 5.76 \text{ J/K}.$$

(c): 1 point

This is the same entropy increase as for the reversible isothermal process, although in this case the system absorbed no heat from the environment.