Homework #7

1. (Kittel 6.4) ***Energy of gas of extreme relativistic particles.*** Extreme relativistic particles have momenta p such that $pc >> Mc^2$, 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 $\varepsilon \cong pc$ in contrast to $\frac{3}{2}\tau$ for the nonrelativistic problem. (An interesting variety of relativistic problems are discussed by E. Fermi in Notes on Thermodynamics and Statistics, University of Chicago Press, 1966, paperback.)

   Solution.

$$\langle\varepsilon\rangle = \frac{\int_0^\infty \varepsilon D(\varepsilon) e^{-\beta\varepsilon} d\varepsilon}{\int_0^\infty D(\varepsilon) e^{-\beta\varepsilon} d\varepsilon}$$

   For $\varepsilon \cong pc$, $D(\varepsilon) \propto \varepsilon^2$. Hence

$$\langle\varepsilon\rangle = \frac{\int_0^\infty \varepsilon\varepsilon^2 e^{-\beta\varepsilon} d\varepsilon}{\int_0^\infty \varepsilon^2 e^{-\beta\varepsilon} d\varepsilon}$$

   Let $x = \beta\varepsilon = \varepsilon/k_B T$. Then

$$\langle\varepsilon\rangle = k_B T \frac{\int_0^\infty x^3 e^{-x} dx}{\int_0^\infty x^2 e^{-x} dx} = k_B T \frac{3\times 2}{2\times 1} = 3k_B T$$

2. (Kittel 6.5) ***Integration of the thermodynamic identity for an ideal gas.*** From the thermodynamic identity at a constant number of particles we have

$$d\sigma = \frac{dU}{\tau} + \frac{pdV}{\tau} = \frac{1}{\tau}\left(\frac{\partial U}{\partial \tau}\right)_V d\tau + \frac{1}{\tau}\left(\frac{\partial U}{\partial V}\right)_\tau dV + \frac{pdV}{\tau}$$

   Show by integration that for an ideal gas the entropy is

$$\sigma = C_V \log\tau + N\log V + \sigma_1$$

   where σ_1 is a constant independent of τ and V.

Solution.

$$d\sigma = \frac{1}{\tau}\left(\frac{\partial U}{\partial \tau}\right)_V d\tau + \frac{1}{\tau}\left(\frac{\partial U}{\partial V}\right)_\tau dV + \frac{pdV}{\tau}$$

For an ideal gas, $pV = Nk_BT = N\tau$.

$$\left(\frac{\partial U}{\partial V}\right)_\tau = T\left(\frac{\partial S}{\partial V}\right)_\tau - p = T\left(\frac{\partial p}{\partial T}\right)_V - p = T\frac{Nk_B}{V} - p = 0$$

$$d\sigma = \frac{1}{\tau}\left(\frac{\partial U}{\partial \tau}\right)_V d\tau + \frac{pdV}{\tau} = \frac{C_V}{\tau}d\tau + \frac{N}{V}dV$$

$$\sigma = \int \frac{C_V}{\tau}d\tau + \frac{N}{V}dV = C_V \ln \tau + N \ln V + \sigma_1$$

3. (Kittel 6.7) ***Relation of pressure and energy density.***

(a) Show that the average pressure in a system in thermal contact with a heat reservoir is given by

$$p = -\frac{\sum_s (\partial \varepsilon_s / \partial V)_N \exp(-\varepsilon_s / \tau)}{Z}$$

where the sum is over all states of the system.

(b) Show for a gas of free particles that

$$\left(\frac{\partial \varepsilon_s}{\partial V}\right)_N = -\frac{2}{3}\frac{\varepsilon_s}{V}$$

as a result of the boundary conditions of the problem. The result holds equally well whether ε_s refers to a state of N noninteracting particles or to an orbital.

(c) Show that for a gas of free non-relativistic particles

$$p = 2U/3V$$

where U is the thermal average energy of the system. The result is not limited to the classical regime; it holds equally well for fermion and boson particles, as long as they are nonrelativistic.

Solution.

$$p = -\frac{1}{Z}\sum_s \left(\frac{\partial \varepsilon_s}{\partial V}\right)_N e^{-\varepsilon_s/\tau}$$

$$\varepsilon_s = \frac{\hbar^2}{2m} k_s{}^2 \text{ with } k_s \approx \frac{1}{L} = \frac{1}{V^{1/3}}$$

$$\varepsilon_s \propto \frac{1}{V^{2/3}}$$

Let $\varepsilon_s \propto \frac{A_s}{V^{2/3}}$. Then

$$\frac{\partial \varepsilon_s}{\partial V} = -\frac{2}{3}\frac{A_s}{V^{5/3}} = -\frac{2}{3}\frac{\varepsilon_s}{V}$$

$$p = \frac{2}{3}\frac{1}{Z}\sum_s \frac{\varepsilon_s}{V} e^{-\varepsilon_s/\tau} = \frac{2}{3V}\frac{1}{Z}\sum_s \varepsilon_s e^{-\varepsilon_s/\tau} = \frac{2U}{3V}$$

4. (Kittel 6.9) ***Gas of atoms with internal degrees 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) chemical potential; (b) free energy; (c) entropy; (d) pressure; (e) heat capacity at constant pressure.

Solution.

$$N = \lambda \sum_\varepsilon e^{-\beta\varepsilon}$$

$$\varepsilon = \frac{p^2}{2m} + \varepsilon_{\text{int}}$$

$$\varepsilon_{\text{int}} = 0 \Rightarrow \sum_\varepsilon e^{-\beta\varepsilon} = Z = Vn_Q$$

$$\varepsilon_{\text{int}} = \Delta \Rightarrow \sum_\varepsilon e^{-\beta\varepsilon} = e^{-\beta\Delta} Z = Vn_Q e^{-\beta\Delta}$$

$$N = \lambda \sum_{\varepsilon} e^{-\beta\varepsilon} = \lambda V n_Q \left(1 + e^{-\beta\Delta}\right)$$

$$\lambda = \frac{n}{n_Q} \frac{1}{1 + e^{-\beta\Delta}}$$

$$\lambda = e^{\mu/\tau}$$

$$\mu = \tau \ln \frac{n}{n_Q} - \tau \ln\left(1 + e^{-\beta\Delta}\right)$$

(b)

$$Z_1 = \left(1 + e^{-\beta\Delta}\right) Z_{ideal} = \left(1 + e^{-\beta\Delta}\right) V n_Q$$

$$Z = \frac{Z_1^{\,N}}{N!} = \frac{(V n_Q)^N}{N!} \left(1 + e^{-\beta\Delta}\right)^N$$

$$F = -\tau \ln Z = -\tau \ln\left(\frac{V n_Q}{N!}\right)^N - N\tau \ln\left(1 + e^{-\beta\Delta}\right) = N\tau \left(\ln \frac{n}{n_Q} - 1\right) - N\tau \ln\left(1 + e^{-\beta\Delta}\right)$$

(c)

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_V = N\left[\ln \frac{n_Q}{n} + \frac{5}{2}\right] + N \ln\left(1 + e^{-\beta\Delta}\right) + N\tau \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \frac{\Delta}{\tau^2}$$

$$\text{ie.} \quad \sigma = N\left[\ln \frac{n_Q}{n} + \frac{5}{2}\right] + N \ln\left(1 + e^{-\beta\Delta}\right) + \frac{N\Delta}{\tau} \frac{1}{e^{\beta\Delta} + 1}$$

(d)

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

(e)

$$C_p = \tau\left(\frac{\partial \sigma}{\partial T}\right)_p = k_B \tau \left(\frac{\partial \sigma}{\partial \tau}\right)_p = k_B \tau \frac{\partial}{\partial \tau} N\left(\ln \frac{n_Q}{n} + \frac{5}{2}\right) + k_B \tau \frac{\partial}{\partial \tau}\left(N \ln(1 + e^{-\beta\Delta}) + \frac{N\Delta}{\tau} \frac{1}{e^{\beta\Delta} + 1}\right)$$

Hence,

$$C_p = \frac{5}{2}Nk_B + Nk_B\tau\left(\frac{e^{-\beta\Delta}}{1+e^{-\beta\Delta}}\frac{\Delta}{\tau^2} - \frac{1}{e^{\beta\Delta}+1}\frac{\Delta}{\tau^2} + \frac{\Delta}{\tau}\frac{e^{\beta\Delta}}{(e^{\beta\Delta}+1)^2}\frac{\Delta}{\tau^2}\right) = \frac{5Nk_B}{2} + Nk_B\frac{\Delta^2}{\tau^2}\frac{e^{\beta\Delta}}{(e^{\beta\Delta}+1)^2}$$

5. (Kittel 6.11) ***Convective isentropic equilibrium of the atmosphere.*** The lower 10-15 km of the atmosphere - the troposphere -is often in a convective steady state at constant entropy, not constant temperature. In such equilibrium pV^γ is independent of altitude, where $\gamma = C_p/C_V$. Use the condition of mechanical equilibrium in a uniform gravitational field to: (a) Show that $dT/dz = \text{constant}$, where z is the altitude. This quantity, important in meteorology, is called the dry adiabatic lapse rate. (Do not use the barometric pressure relation that was derived in Chapter 5 for an isothermal atmosphere.) (b) Estimate dT/dz, in degrees Celsius per km. Take $\gamma = 7/5$. (c) Show that $p \propto \rho^\gamma$, where ρ is the mass density. If the actual temperature gradient is greater than the isentropic gradient, the atmosphere may be unstable with respect to convection.

<u>Solution</u>.

(a)

$$[p(z) - p(z+dz)]A = nmAdzg \Rightarrow -\frac{dp}{dz} = nmg$$

$$\frac{dT}{dz} = \frac{dT}{dp}\frac{dp}{dz} = -\frac{dT}{dp}nmg \quad \text{(Eqn 1)}$$

$$pV^\gamma = \text{constant, with } pV = Nk_BT \text{ gives } \mathrm{p}\left(\frac{\mathrm{T}}{\mathrm{p}}\right)^\gamma = \text{constant and so } \frac{T^\gamma}{p^{\gamma-1}} = \text{constant}$$

$$\ln\frac{T^\gamma}{p^{\gamma-1}} = \text{constant} \Rightarrow \gamma\ln T - (\gamma-1)\ln p = \text{constant}$$

$$\frac{\gamma}{T}dT - (\gamma-1)\frac{dp}{p} = 0$$

$$\frac{dT}{dp} = \frac{(\gamma-1)T}{\gamma p} \quad \text{(Eqn 2)}$$

Eqn 2 can also be obtained from

$$\tau d\sigma = dU + pdV = c_V dT + pdV$$

For isentropic processes $d\sigma = 0$ and so

$$C_V dT + pdV = 0$$

$$pdV + Vdp = Nk_B dT$$

$$C_V dT + Nk_B dT - Vdp = 0$$

$$C_p dT - \frac{Nk_B T}{p} dp = 0$$

(since $\gamma = \frac{C_p}{C_V}$ and $Nk_B = C_p - C_V$).

$$\gamma dT - (\gamma - 1)\frac{Tdp}{p} = 0 \Rightarrow \frac{dT}{dp} = \frac{\gamma - 1}{\gamma}\frac{T}{p}$$

Substitute Eqn 2 into Eqn 1 to get

$$\frac{dT}{dz} = -\frac{\gamma - 1}{\gamma}\frac{Tp}{p} mg$$

Now $p = nk_B T$ and so

$$\frac{dT}{dz} = -\frac{\gamma - 1}{\gamma}\frac{mg}{k_B} = \text{constant}$$

(b)

Take m the mass of N_2

$$m = 28 \times 1.67 \times 10^{-27} kg = 4.68 \times 10^{-26} kg$$

Now $\gamma = \frac{7}{5}$ and so

$$\frac{dT}{dz} = -\frac{7/5-1}{7/5}\frac{4.68\times10^{-26}}{1.38\times10^{-23}}9.8K/m = 9.5\times10^{-3}\,K/m$$

T drops about 10 degrees Celsius every km.

(c)

$$pV^{\gamma} = \text{ constant, and } \rho \propto V^{-1} \Rightarrow p\rho^{-\gamma} = \text{ constant, and so } p \propto \rho^{\gamma}$$

6. (Kittel 6.12) ***Ideal gas in two dimensions.*** (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. (b) Find an expression for the energy U of the gas. (c) find an expression for the entropy σ. The temperature is τ.

Solution.

(a) $N = \lambda Z_1$ with $Z_1 = \sum e^{-\beta\varepsilon} = \int D(\varepsilon)e^{-\beta\varepsilon}d\varepsilon$.

$$D(\varepsilon)d\varepsilon = \frac{A2\pi pdp}{h^2} = \frac{2\pi A}{h^2}\frac{1}{2}dp^2 = \frac{2\pi Am}{h^2}d\varepsilon$$

$$Z_1 = \frac{2\pi Am}{h^2}\int_0^{\infty} e^{-\beta\varepsilon}d\varepsilon = \frac{2\pi Am}{h^2}\tau$$

$$N = e^{\mu/\tau}\frac{2\pi Am}{h^2}\tau \Rightarrow \mu = \tau\ln\frac{Nh^2}{2\pi Am\tau}$$

(b)

$$\bar{\varepsilon} = \frac{1}{2}k_BT + \frac{1}{2}k_BT = k_BT$$

$$U = N\bar{\varepsilon} = Nk_BT$$

(c)

$$Z = \frac{Z_1^{\,N}}{N!} \Rightarrow F = -\tau\ln Z = -\tau\left(N\ln\left(\frac{2\pi Am}{h^2}\tau\right) - N\ln N + N\right)$$

$$F = -\tau N\left(\ln\frac{2\pi Am\tau}{h^2 N} + 1\right)$$

$$\sigma = -\left(\frac{\partial F}{\partial \tau}\right)_A = N\left(\ln\frac{2\pi Am\tau}{h^2 N} + 1\right) + N\tau\frac{1}{\tau} = N\left(\ln\frac{2\pi Am\tau}{h^2 N} + 2\right)$$

$$U = F + \tau\sigma = N\tau$$