

— **Physics 215A HW1: Review of Thermodynamics**

1. Problem 1

- (a) Establish thermodynamically the following formulas,

$$\left(\frac{\partial P}{\partial T}\right)_\mu = \frac{S}{V}$$

$$\left(\frac{\partial P}{\partial \mu}\right)_T = \frac{N}{V}$$

- (b) For an ideal gas whose internal energy is given by $E = cNkT$, for some positive constant c , use the above formulas to obtain the dependence of the pressure P on the temperature T and the chemical potential μ , up to an overall integration constant that is independent of μ and T . (Compare your result with the Sackler-Tetrode formula in the case of $c = 3/2$.)

My Solution

- (a) Start from square one (the work I am doing here was me trying to solve it a different way than using the Gibbs-Duhem relation, then I stopped trying to solve it this way, and resorted using G-D relation. I am leaving the result of the differential of the gibbs energy for fun):

$$dN = 0$$

$$dE = \delta Q - \delta W$$

$$\delta Q = TdS$$

$$\delta W = PdV - Nd\mu$$

$$dE = TdS - (PdV - Nd\mu) = TdS - PdV + Nd\mu$$

Transform this (definitely not the Gibbs free energy), then take the differential of it:

$$G = E - TS + PV$$

$$dG = dE - TdS - SdT + PdV + VdP = Nd\mu + VdP - SdT$$

Using the Gibbs-Duhem:

$$0 = SdT - VdP + Nd\mu$$

$$dP = \frac{S}{V}dT + \frac{N}{V}d\mu$$

and knowing that a total differential can be split into its partials as:

$$dP = \left(\frac{\partial P}{\partial T}\right)_\mu dT + \left(\frac{\partial P}{\partial \mu}\right)_T d\mu$$

Then simply equating coefficients lets us show that both:

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_\mu = \frac{S}{V}}$$

$$\boxed{\left(\frac{\partial P}{\partial \mu}\right)_T = \frac{N}{V}}$$

(b) Since

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T}(cNkT) = cNk$$

Fixing μ and V , and knowing that $dE = C_V dT$ for an ideal gas:

$$dE = TdS = C_V dT = cNkdT = (dE)_{V,\mu}$$

separating variables then integrating:

$$\begin{aligned}\int dS &= cNk \int \left(\frac{dT}{T}\right) \\ S &= cNk(\ln T/T_0 + \text{const}) \\ &= cNk \ln T + cNka = cNk \ln(T/T_0) + f(N)\end{aligned}$$

Using the formulas from part a:

$$\left(\frac{\partial P}{\partial T}\right)_\mu = \frac{1}{V}(cNk \ln(T/T_0) + f(N)) = \frac{cNk}{V} \ln(T/T_0) + h(N, V)$$

and also:

$$\left(\frac{\partial P}{\partial \mu}\right)_T = \frac{N}{V}$$

Knowing both partials, we can reconstruct $P(\mu, T)$:

$$\begin{aligned}P(\mu, T) &= \int \frac{\partial P}{\partial \mu} d\mu + \int f'(T) dT = \frac{N\mu}{V} + \int \left(\frac{cNk}{V} \ln(T/T_0) + h(N, V)\right) dT \\ &= \frac{N\mu}{V} + \frac{cNk}{V}(T \ln(T/T_0) - T + c_1) + h(N, V)T \\ &= \frac{N\mu}{V} + \frac{cNk}{V}(T \ln(T/T_0) + c_1) + u(N, V)T\end{aligned}$$

Thus we have shown the dependence of P on μ and T , with an integration constant independent of μ and T :

$$P(\mu, T) = \frac{N\mu}{V} + \frac{cNk}{V}(T \ln(T/T_0) + c_1) + u(N, V)T$$

and comparing with the sackler-tetrode formula while $c = 3/2$:

$$P(\mu, T) = \frac{N\mu}{V} + \frac{3Nk}{2V}(T \ln(T) + c_1) + u(N, V)T = \frac{N\mu}{V} + \frac{3Nk}{2V} \ln(T) + u(N, V)T + c_2$$

2. Problem 2

A hard core gas obeys the equation of state $P(V - Nb) = NkT$, and has a temperature independent heat capacity C_V . Throughout, N and b are constant.

(a) Find the Maxwell relation involving $\frac{\partial S}{\partial V}$ at fixed T and N

(b) By calculating $dE(T, V)$, show that E is a function of T only

(c) Show that $\gamma = \frac{C_P}{C_V}$ is given by $\gamma = 1 + \frac{Nk}{C_V}$, and independent of T and V

(d) By writing an expression for $E(P, V)$, or otherwise, show that an adiabatic change must satisfy the equation $P(V - Nb)^\gamma = \text{constant}$

My Solution

(a) I derived the Gibbs differential in number 1 from scratch, and instead of repeating a similar derivation for the Helmholtz Free Energy, I just state it:

$$dF = -SdT - PdV$$

Where this is of course understood to have N fixed.

Since F is a function of both T and V, and by Clairaut's theorem of second order partial derivatives:

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right)_{T,N} = \left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right)_{V,N}$$

Then finding these partials explicitly:

$$\begin{aligned}\left(\frac{\partial F}{\partial T}\right)_V &= -S \\ \left(\frac{\partial F}{\partial V}\right)_T &= -P\end{aligned}$$

Combining gives Maxwell's relation:

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$$

Then using the hardcore ideal gas law to find this explicitly:

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial}{\partial T}\left(\frac{NkT}{(V-Nb)}\right)\right)_{V,N} = \frac{Nk}{V-Nb} \implies \boxed{\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{Nk}{V-Nb}}$$

- (b) Just as in problem 1, I start with the first law of thermodynamics for an isolated and closed system:

$$dE = \delta Q - \delta W$$

$$\delta Q = TdS$$

$$\delta W = PdV$$

$$dE = TdS - PdV = TdS - \left(\frac{NkT}{(V-Nb)}\right)dV$$

I then take the differential of the entropy to attempt an elimination of everything that is not dT:

$$dS = \frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial V}dV = \left(\frac{\partial S}{\partial T}\right)_{V,N}dT + \left(\frac{\partial S}{\partial V}\right)_{T,N}dV$$

But we know both of these partial derivatives. Namely, one from part a and one from the definition of specific heat for an internal energy which might vary with V and T (D'Hoker 2.26):

$$\implies dS = (C_V/T)dT + \frac{Nk}{V-Nb}dV$$

Plug this guy back into the equation for dE:

$$dE = TdS - \left(\frac{NkT}{(V-Nb)}\right)dV = T\left((C_V/T)dT + \frac{Nk}{V-Nb}dV\right) - \left(\frac{NkT}{(V-Nb)}\right)dV$$

Which then makes it obvious that E only depends on T:

$$\boxed{dE = C_V dT}$$

- (c) Here I make use of D'Hoker's results at 2.27:

$$C_P = \left(\frac{\partial E}{\partial T}\right)_{P,N} + P\left(\frac{\partial V}{\partial T}\right)_{P,N} = C_V + P\frac{\partial}{\partial T}\left(\frac{NkT}{P} + bN\right) = C_V + Nk$$

Which then just begs for the ratio to be taken:

$$\gamma = \frac{C_P}{C_V} = \frac{C_V + Nk}{C_V} = 1 + \frac{Nk}{C_V}$$

Thus:

$$\boxed{\gamma = C_P/C_V = 1 + Nk/C_V}$$

- (d) Due to being adiabatic $\delta Q = 0$, so:

$$dE = \delta Q - \delta W = -\delta W = -PdV$$

From part a:

$$dE = C_V dT = -PdV \\ \implies C_V dT + PdV = C_V dT + \frac{NkT}{V-Nb} dV = 0$$

$$-\frac{dT}{T} = \frac{Nk}{C_V(V-Nb)} dV = (\gamma - 1) \frac{dV}{V-Nb}$$

Integrating:

$$\ln(T) = (1 - \gamma) \ln(V - Nb)$$

$$\ln T = \ln(V - Nb)^{1-\gamma}$$

$$T = (V - Nb)^{1-\gamma}$$

From problem statement:

$$T = \frac{P}{Nk}(V - Nb)$$

Combining:

$$\frac{P}{Nk}(V - Nb) = (V - Nb)^{1-\gamma} \implies \frac{P}{Nk} = (V - Nb)^{-\gamma}$$

and since N and k are of course both constants, we can conclude the result we wanted:

$$\boxed{P(V - Nb)^\gamma = \text{constant}}$$

3. Problem 3

- (a) From the first law of thermodynamics, derive the following relation between the pressure P and internal energy E , both of which are functions of T, V ,

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

- (b) Consider a thermodynamic system whose equation of state is given by $P = \alpha\epsilon(T)$, where α is a constant while its internal energy is given by $E = V\epsilon(T)$, for the same function $\epsilon(T)$. Calculate the temperature dependence of E .
- (c) Calculate the entropy $S(T, V)$ for the system whose equation of state is given above.

My Solution

- (a) Starting with the first law at fixed N:

$$dE = TdS - PdV$$

I differentiate in V:

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Then in T:

$$\left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Then using the free energy:

$$F = E - TS$$

$$dF = d(E - TS) = dE - SdT - TdS = (\mathcal{T}d\mathcal{S} - PdV) - SdT - \mathcal{T}d\mathcal{S} = -SdT - PdV$$

Since F is a function of both T and V , and by Clairaut's theorem of second order partial derivatives:

$$\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)_T$$

Where I then express the two partials using the result of the free energy obtained earlier:

$$\begin{aligned} \left(\frac{\partial F}{\partial T} \right)_V &= \frac{\partial}{\partial T} (-SdT - Pd\mathcal{W})_V = -S \\ \left(\frac{\partial F}{\partial V} \right)_T &= \frac{\partial}{\partial V} (-SdT - PdV)_T = -P \end{aligned}$$

Finally,

$$\frac{\partial}{\partial V} (-S) = \frac{\partial}{\partial T} (-P) \longrightarrow \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

Which is enough to recover the desired result:

$$\boxed{\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P}$$

(b) Here I use the results from part a:

$$\left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P = T \left(\alpha \frac{\partial \epsilon(T)}{\partial T} \right)_V - \alpha \epsilon(T)$$

Then computing the same quantity, except directly from the E we were given:

$$\left(\frac{\partial E}{\partial V} \right)_T = \epsilon(T)$$

Equating, then integrating the differential equation:

$$\epsilon(T) = T \left(\alpha \frac{\partial \epsilon(T)}{\partial T} \right)_V - \alpha \epsilon(T)$$

$$\epsilon(T)(1 + \alpha) = T \alpha \frac{\partial \epsilon(T)}{\partial T}$$

$$\implies \epsilon(T) = \epsilon(0) T^{\frac{\alpha+1}{\alpha}}$$

since the problem asked for $E(T)$:

$$\boxed{E(T) = V \epsilon(T) = V \epsilon(0) T^{\frac{\alpha+1}{\alpha}}}$$

(c) Using this sucker from part a:

$$\left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$V \frac{\partial \epsilon(T)}{\partial T} = V \frac{\alpha+1}{\alpha} \epsilon(0) T^{1/\alpha} = T \frac{\partial S}{\partial T}$$

$$\implies \frac{\alpha+1}{\alpha} V \epsilon(0) T^{\frac{1-\alpha}{\alpha}} = \frac{\partial S}{\partial T} \implies \frac{\alpha+1}{\alpha} V \epsilon(0) \int_0^T T^{\frac{1-\alpha}{\alpha}} dT = \int_{S_0}^{S(T,V)} dS$$

Integrating and re-arranging gives:

$$\boxed{S(T, V) = (\alpha + 1) V \epsilon(0) T^{1/\alpha} + S_0}$$

— **Physics 215A: Statistical Mechanics**

Problem 1 (Kardar I, p 32, problem 9)

Some metals become superconducting at low temperature T and low magnetic field B . The heat capacity in the superconducting phase C_s , and in the normal phase C_n may be approximated by,

$$C_s = V\alpha T^3$$

$$C_n = V(\beta T^3 + \gamma T)$$

where V is the volume, and α, β, γ are constants. There is no appreciable change in volume during the transition, so that mechanical work may be ignored.

- (a) Calculate the entropies $S_s(T)$ and $S_n(T)$ at $B = 0$, by making use of the third law of thermodynamics.
- (b) Experiments indicate that the transition is second order, with no latent heat produced. Use this information to obtain the critical temperature T_c as a function of α, β, γ .
- (c) At $T = 0$, the electrons in the superconducting phase condense to form Cooper pairs. As a result, the internal energy in the superconducting phase E_s is reduced by an amount $V\Delta$ compared to the internal energy E_n in the normal phase, so that we have $E_s(T = 0) = E_n(T = 0) - \Delta V$ with positive energy gap Δ . Calculate the internal energies in both phases at finite temperature.
- (d) By comparing the Gibbs free energies in the two phases, obtain Δ in terms of α, β, γ .
- (e) In the presence of a magnetic field B , magnetic work is included by the modification $dE = TdS + BdM$, where M is the magnetization. Thanks to the Meissner effect, the superconducting phase is a perfect diamagnet, and expels completely the magnetic field in its bulk, so that we have $M_s = -\frac{VB}{4\pi}$, in appropriate units. We assume that the normal metal is non-magnetic, so that we have $M_n = 0$. Use this information, in conjunction with the preceding result, to show that the superconducting phase becomes normal for magnetic field larger than B_c , with

$$B_c(T) = B_0 \left(1 - \frac{T^2}{T_0^2} \right)$$

giving an expression for B_0 .

My Solution

- (a) Given that the volume is fixed, we can use the definition of fixed volume specific heat and integrate in both phases:

$$\frac{1}{T}C_V = \left(\frac{\partial S}{\partial T} \right)_{V,N}$$

$$\left(\frac{\partial S}{\partial T} \right)_{V,N} = \frac{1}{T}V\alpha T^3 \implies S_s(T) = \frac{1}{3}V\alpha T^3 + S_s(0)$$

$$\text{Likewise, } \left(\frac{\partial S}{\partial T} \right)_{V,N} = \frac{1}{T}V(\beta T^3 + \gamma T) \implies S_n(T) = V\left(\frac{1}{3}\beta T^3 + \gamma T\right) + S_n(0)$$

- (b) Here I invoke a D'hoker result from chapter 9, equation 9.8 for latent heat. The latent heat transfer between phases is simply the temperature at which the phase transition occurs, scaled by the difference in the entropies of the unique states evaluated at that temperature. The problem statement says this heat is zero:

$$Q_{latent} = 0 = T_c[S_s(T_c) - S_n(T_c)] = T_c\left[\frac{1}{3}V\alpha T_c^3 + S_s(0) - \left(V\left(\frac{1}{3}\beta T_c^3 + \gamma T_c\right) + S_n(0)\right)\right]$$

Assuming $S_s(0) = S_n(0) = 0$

$$0 = T_c\left[\frac{1}{3}V\alpha T_c^3 - \frac{1}{3}V\beta T_c^3 - V\gamma T_c\right] = \frac{1}{3}VT_c^2(\alpha - \beta) - V\gamma$$

$$\longrightarrow \gamma = \frac{1}{3}T_c^2(\alpha - \beta)$$

Where then clearly,

$$T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}}$$

- (c) Invoking 2.27 of D'hoker's notes for constant volume:

$$C_v = \left(\frac{\partial E}{\partial T}\right)_{V,N} \longrightarrow dE = C dT$$

for the normal phase case:

$$\int dE = \int C dT = \int V(\beta T^3 + \gamma T) dT$$

$$E_n(T) - E_n(0) = V\left(\frac{1}{4}\beta T^4 + \frac{1}{2}\gamma T^2\right)$$

$$E_n(T) = V\left(\frac{1}{4}\beta T^4 + \frac{1}{2}\gamma T^2\right) + E_n(0)$$

Likewise for the superconducting phase,

$$\int dE = \int C dT = \int V\alpha T^3 dT$$

$$E_s(T) - E_s(0) = \frac{1}{4}V\alpha T^4$$

And using the initial energy given for the superconducting state in terms of the initial energy of the normal state,

$$E_s(T) - (E_n(0) - \Delta V) = \frac{1}{4}V\alpha T^4$$

$$E_s(T) = E_n(0) - \Delta V + \frac{1}{4}V\alpha T^4$$

- (d) Extending the idea of the Helmholtz free energy by including a generalized conjugate term with a force and displacement, we can construct one for the presence of a magnetic field:

$$G = E - TS - fX$$

$$G = E - TS - BM - \mu N \longrightarrow G = E - TS - BM = \mu N$$

Where B represents the magnetic field and M represents the magnetization. Knowing B=0, we can simplify. Doing first the normal state:

$$G_n = E_n(T) - TS_n(T) = VT\left(\frac{1}{4}\beta T^3 + \frac{1}{2}\gamma T\right) + E_n(0) - VT\left(\frac{1}{3}\beta T^3 + \gamma T\right)$$

$$G_n = VT\left(\frac{1}{4}\beta T^3 + \frac{1}{2}\gamma T - \frac{1}{3}\beta T^3 - \gamma T\right) + E_n(0) = VT\left(-\frac{1}{12}\beta T^3 - \frac{1}{2}\gamma T\right) + E_n(0) = \mu_n N_n$$

so,

$$G_n = -VT\left(\frac{1}{12}\beta T^3 + \frac{1}{2}\gamma T\right) + E_n(0)$$

Likewise,

$$G_s = E_s(T) - TS_s(T) = E_n(0) - \Delta V + \frac{1}{4}V\alpha T^4 - T\left(\frac{1}{3}V\alpha T^3\right)$$

$$G_s = E_n(0) + V[-\Delta + \frac{1}{4}\alpha T^4 - \frac{1}{3}\alpha T^4] = E_n(0) + V[-\Delta - \frac{1}{12}\alpha T^4]$$

hence,

$$G_s = E_n(0) - V[\Delta + \frac{1}{12}\alpha T^4] = \mu_s N_s$$

Here I make an argument for equating the Gibbs free energies. Since $G_i = \mu_i N_i$ for the two states, since no exchange of particles, and since the chemical potentials are equal between phase transitions,

$$G_s = G_n \longrightarrow E_n(0) - V[\Delta + \frac{1}{12}\alpha T^4] = -VT(\frac{1}{12}\beta T^3 + \frac{1}{2}\gamma T) + E_n(0)$$

$$\begin{aligned} [\Delta + \frac{1}{12}\alpha T^4] &= T(\frac{1}{12}\beta T^3 + \frac{1}{2}\gamma T) \\ \Delta &= T(\frac{1}{12}\beta T^3 + \frac{1}{2}\gamma T) - \frac{1}{12}\alpha T^4 = \frac{1}{12}\beta T^4 + \frac{1}{2}\gamma T^2 - \frac{1}{12}\alpha T^4 \end{aligned}$$

Therefore,

$$\Delta = \frac{1}{12}T^4(\beta - \alpha) + \frac{1}{2}\gamma T^2$$

evaluating at the temperature the phase transition occurs,

$$\begin{aligned} \Delta &= \frac{1}{12} \left(\sqrt{\frac{3\gamma}{\alpha-\beta}} \right)^4 (\beta - \alpha) + \frac{1}{2}\gamma \left(\sqrt{\frac{3\gamma}{\alpha-\beta}} \right)^2 = \frac{1}{12} \left(\frac{3\gamma}{\alpha-\beta} \right)^2 (\beta - \alpha) + \frac{1}{2} \frac{3\gamma^2}{\alpha-\beta} \\ &= -\frac{3}{4} \frac{\gamma^2}{\alpha-\beta} + \frac{3}{2} \frac{\gamma^2}{\alpha-\beta} = \frac{3}{4} \frac{\gamma^2}{\alpha-\beta} \end{aligned}$$

Therefore, $\Delta = \frac{3}{4} \frac{\gamma^2}{\alpha - \beta}$

(e) Including the magnetic term instead of omitting it like in previous steps,

$$G = E - TS - BM = \mu N$$

which implies we need the total field, given that we have M:

$$dG = d(E - TS - BM) = dE - TdS - SdT - BdM - MdB$$

$$dG = TdS + BdM - TdS - SdT - BdM - MdB = -SdT - MdB$$

Integrating,

$$-\int MdB = \int \frac{VB}{4\pi} dB = \frac{VB}{4\pi} \int B dB = \frac{VB^2}{8\pi}$$

Adding this contribution to the Gibbs free energy,

$$G_n = E_n - TS_n - BM_n = -VT(\frac{1}{12}\beta T^3 + \frac{1}{2}\gamma T) + E_n(0)$$

Likewise,

$$G_s = E_s - TS_s - BM_s = E_n(0) - V[\Delta + \frac{1}{12}\alpha T^4] - \frac{VB^2}{8\pi}$$

Again,

$$G_n = G_s \longrightarrow -VT(\frac{1}{12}\beta T^3 + \frac{1}{2}\gamma T) + E_n(0) = E_n(0) - V[\Delta + \frac{1}{12}\alpha T^4] - \frac{VB^2}{8\pi}$$

$$T(\frac{1}{12}\beta T^3 + \frac{1}{2}\gamma T) = [\Delta + \frac{1}{12}\alpha T^4] + \frac{B^2}{8\pi}$$

$$\begin{aligned} \frac{B^2}{8\pi} &= \frac{1}{12}\beta T^4 + \frac{1}{2}\gamma T^2 - \Delta - \frac{1}{12}\alpha T^4 = \frac{T^4}{12}(\beta - \alpha) + \frac{1}{2}\gamma T^2 - \frac{3}{4} \frac{\gamma^2}{\alpha-\beta} \\ &= \frac{\alpha-\beta}{12} \left[T^4 - \frac{6\gamma}{\alpha-\beta} T^2 + \left(\frac{3\gamma}{\alpha-\beta} \right)^2 \right] = \frac{\alpha-\beta}{12} [T^4 - 2T_c^2 T^2 + T_c^4] = \frac{\alpha-\beta}{12} [(T^2 - T_c^2)^2] = \frac{\alpha-\beta}{12} [(T_c^2 - T^2)^2] \\ &= \frac{\alpha-\beta}{12} T_c^4 \left[(1 - T^2/T_c^2)^2 \right] \end{aligned}$$

solving for B

$$B = \sqrt{8\pi \frac{\alpha-\beta}{12} T_c^4 \left[(1 - T^2/T_c^2)^2 \right]} = \sqrt{\frac{2\pi}{3} (\alpha - \beta) T_c^2 (1 - T^2/T_c^2)} = \boxed{B_0 (1 - T^2/T_c^2)}$$

$$\text{with } B_0 = \sqrt{\frac{2\pi}{3} (\alpha - \beta) T_c^2}$$

Problem 2 (Pathria problem 1.7)

Study the statistical mechanics of an ultra-relativistic gas characterized by the following single-particle energy relation for the states,

$$\epsilon(n_x, n_y, n_z) = \frac{\pi \hbar c}{L} (n_x^2 + n_y^2 + n_z^2)^{\frac{1}{2}}$$

with n_x, n_y, n_z , integers, instead of the non-relativistic law of (1.4.5) of Pathria, along the lines of section 1.4 of Pathria. Show that the ratio C_P/C_V in this case equals $4/3$.

My Solution

1. I will need the definition of the Beta function:

$$B(x, y) = \int_0^1 z^{x-1} (1-z)^{y-1} dz = \frac{\Gamma(x)\Gamma(y)}{\Gamma(x+y)}$$

as well as these guys:

$$T = \left(\frac{\partial E}{\partial S} \right)_{N, V}$$

$$C_P = \left(\frac{\partial (E + PV)}{\partial T} \right)_{P, N}$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{V, N}$$

$$P = - \left(\frac{\partial E}{\partial V} \right)_{N, S}$$

From problem statement,

$$(n_x^2 + n_y^2 + n_z^2)^{\frac{1}{2}} = \frac{L}{\pi \hbar c} \epsilon = \frac{2V^{1/3} \epsilon}{\hbar c}$$

$$n_x^2 + n_y^2 + n_z^2 = \left(\frac{V^{1/3} \epsilon}{\pi \hbar c} \right)^2 = \frac{4V^{2/3} \epsilon^2}{(\hbar c)^2} = \epsilon^*$$

Summing this over all particles,

$$\sum_{r=1}^{3N} n_r^2 = \frac{4V^{2/3} E^2}{(\hbar c)^2} = E^*$$

The combination of $V^{2/3} E^2$ will show up in our definition of entropy like so: $S(N, V^{2/3} E^2)$

We are after a number $\Sigma(E^*)$ which asymptotically approaches the volume of a 3N dimensional sphere with radius $\sqrt{E^*}$, to which I invoke the following result courtesy of Pathria and Beale's appendix C:

$$V_{3N}(\sqrt{E^*}) = \frac{\pi^{3N/2}}{(3N/2)!} E^{*3N/2}$$

$$\Sigma_N(E^*) \approx \left(\frac{1}{2} \right)^{3N} V_{3N}(\sqrt{E^*}) = \left(\frac{1}{2} \right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} E^{*3N/2}$$

$$\text{evaluating at } E^* = \frac{4V^{2/3} E^2}{(\hbar c)^2},$$

$$\Sigma_N(E) \approx \left(\frac{1}{2} \right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} \left(\frac{4V^{2/3} E^2}{(\hbar c)^2} \right)^{3N/2} = \left[\frac{\pi^{3/2} E^3 V}{(\hbar c)^3} \right]^N \frac{1}{(3N/2)!} = [\alpha E^3 V]^N \frac{1}{(3N/2)!}$$

$$\text{Where I have defined } \alpha = \frac{\pi^{3/2}}{(\hbar c)^3}$$

Logging both sides and assuming this gas has many particles with Stirling's formula,
 $\ln N! = N \ln N - N$

$$S/k \approx \ln [\Sigma_N(E)] \approx \ln \left[(\alpha E^3 V)^N \right] - \left[\frac{3N}{2} \ln \left(\frac{3N}{2} \right) - \frac{3N}{2} \right]$$

$$\begin{aligned} S(N, V, E) &= k \ln [\Sigma_N(E)] = Nk \ln [(\alpha E^3 V)] - Nk \ln \left[\left(\frac{3N}{2} \right)^{3/2} \right] + \frac{3Nk}{2} \\ &= Nk \ln \left[\frac{\alpha E^3 V}{\left(\frac{3N}{2} \right)^{3/2}} \right] + \frac{3Nk}{2} \end{aligned}$$

I find E from inverting the entropy:

$$E = \left(\frac{1}{\alpha V} \right)^{1/3} \left(\frac{3N}{2} \right)^{-1/2} \exp \left[\frac{S}{3Nk} - \frac{1}{2} \right] = \beta \exp \left[\frac{S}{3Nk} - \frac{1}{2} \right]$$

Where I define $\beta = \left(\frac{1}{\alpha V} \right)^{1/3} \left(\frac{3N}{2} \right)^{-1/2}$

Using the temperature definition, I re-write the exponential in terms of NkT ,

$$\begin{aligned} T &= \left(\frac{\partial E}{\partial S} \right) = \frac{\beta}{3Nk} \exp \left[\frac{S}{3Nk} - \frac{1}{2} \right] \\ \longrightarrow \exp \left[\frac{S}{3Nk} - \frac{1}{2} \right] &= \frac{3NkT}{\beta} \end{aligned}$$

Finally, I can write E in terms of T, N, k only:

$$E = \beta \left[\frac{3NkT}{\beta} \right] = 3NkT$$

Which makes sense, since adding a relativistic addition to the energy of the particles gives them an additional $\frac{1}{2}kT$ of energy per degree of translational degree of freedom.

From E we can construct $\gamma = \frac{C_P}{C_V}$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = 3Nk$$

$$C_P = \left(\frac{\partial (E+PV)}{\partial T} \right)_{P,N} = \left(\frac{\partial (3NkT+NkT)}{\partial T} \right)_{P,N} = 4Nk$$

Therefore finally,

$$\gamma = \frac{4Nk}{3Nk} = \boxed{\frac{4}{3}}$$

Problem 3 (Pathria 3.13)

Consider an ideal gas consisting of N_1 molecules of mass m_1 and N_2 molecules of mass m_2 , confined to a space of volume V . Assume that the molecules of a given kind are mutually indistinguishable, while those of one kind are distinguishable from those of the other kind.

- Evaluate the total number of micro-states $\Omega(E, N_1, N_2)$, the entropy, temperature, and chemical potentials.
- Compare your results with the ones pertaining to an ideal gas with $N_1 + N_2$ molecules, all of one kind and mass m , such that $m(N_1 + N_2) = m_1 N_1 + m_2 N_2$.

My Solution

- Here I make use of the partition function for a single ideal gas made of N particles assuming indistinguishability between members of the same type,

$$Z'_1 = \frac{Z_1^N}{N!}$$

Combining these two independent partition functions to construct a joint partition function:

$$Z = Z'_1 Z'_2 = \frac{Z_1^{N_1}}{N_1!} \frac{Z_2^{N_2}}{N_2!}$$

Then knowing the canonical ensemble partition function of an ideal gas as,

$$Z_1 = \left(\frac{2\pi m_1 kT}{h^2} \right)^{\frac{3}{2}} V$$

We can make the total, then count microstates using it:

$$\begin{aligned} \Omega(E, N_1, N_2) &= Z e^{-\frac{E}{kT}} = \frac{Z_1^{N_1}}{N_1!} \frac{Z_2^{N_2}}{N_2!} e^{-\frac{E}{kT}} = \frac{\left[\left(\frac{2\pi m_1 kT}{h^2} \right)^{\frac{3}{2}} V \right]^{N_1}}{N_1!} \frac{\left[\left(\frac{2\pi m_2 kT}{h^2} \right)^{\frac{3}{2}} V \right]^{N_2}}{N_2!} e^{-\frac{E}{kT}} \\ &= \frac{\left(\frac{2\pi m_1 kT}{h^2} \right)^{\frac{3N_1}{2}} \left(\frac{2\pi m_2 kT}{h^2} \right)^{\frac{3N_2}{2}} V^{N_1} V^{N_2}}{N_1! N_2!} e^{-\frac{E}{kT}} = \boxed{\frac{m_1^{\frac{3N_1}{2}} m_2^{\frac{3N_2}{2}} \left(\frac{2\pi kT}{h^2} \right)^{\frac{3}{2}(N_1+N_2)} e^{-\frac{E}{kT}}}{N_1! N_2!}} \end{aligned}$$

Entropy,

$$\begin{aligned} S &= S_1 + S_2 = k \ln [\Omega(E_1, N_1)] + k \ln [\Omega(E_2, N_2)] = k \ln [\Omega(E, N_1, N_2)] \\ &= k \ln [\Omega(E, N_1, N_2)] = k \ln \left[\frac{m_1^{\frac{3N_1}{2}} m_2^{\frac{3N_2}{2}} \left(\frac{2\pi kT}{h^2} \right)^{\frac{3}{2}(N_1+N_2)} e^{-\frac{E}{kT}}}{N_1! N_2!} \right] \\ &= k \ln \left[m_1^{\frac{3N_1}{2}} m_2^{\frac{3N_2}{2}} \left(\frac{2\pi kT}{h^2} \right)^{\frac{3}{2}(N_1+N_2)} \frac{e^{-\frac{E}{kT}}}{N_1! N_2!} \right] \\ &= \boxed{k \ln \left[\alpha e^{-\frac{E}{kT}} \right]} \text{ Where I have defined } \alpha = \frac{m_1^{\frac{3N_1}{2}} m_2^{\frac{3N_2}{2}} \left(\frac{2\pi kT}{h^2} \right)^{\frac{3}{2}(N_1+N_2)}}{N_1! N_2!} \end{aligned}$$

Solving for the temperature,

$$S = k \ln [\alpha] + k \ln \left[e^{-\frac{E}{kT}} \right] = k \ln [\alpha] - \frac{E}{T}$$

$$\frac{E}{T} = k \ln [\alpha] - S \longrightarrow \boxed{T = \frac{E}{k \ln [\alpha] - S}}$$

Then for each chemical potential,

$$\mu_1 = -kT \ln \left[\frac{\left(\frac{2\pi m_1 kT}{h^2} \right)^{\frac{3}{2}} V}{N_1} \right] = -kT \left(\ln \left[\left(\frac{2\pi m_1 kT}{h^2} \right)^{\frac{3}{2}} V \right] - \ln [N_1] \right) = \boxed{kT \ln [N_1] - kT \ln \left[\left(\frac{2\pi m_1 kT}{h^2} \right)^{\frac{3}{2}} V \right]}$$

Likewise,

$$\boxed{\mu_2 = -kT \ln \left[\left(\frac{2\pi m_2 kT}{h^2} \right)^{\frac{3}{2}} V \right] + kT \ln [N_2]}$$

- (b) Comparing my result to the following results indicates a difference since no particles N_1 and N_2 are distinguishable from each other in the first case, while in the second, they are not since they are again the same type.

The entropy,

$$S = k(N_1 + N_2) \ln \left[\frac{V}{(N_1 + N_2)!} \left(\frac{kT(m_1 N_1 + m_2 N_2)}{2\pi \hbar^2 (N_1 + N_2)} \right)^{3/2} \right] + \frac{5}{2} k(N_1 + N_2)$$

Which is almost the same, except the difference is in the counting of the microstates held in the factorials of the denominators of each entropy. Likewise, the following quantities also change:

$$E = \frac{3\pi \hbar^2 (N_1 + N_2)^{5/3}}{m V^{2/3}} e^{\frac{2S}{3k(N_1 + N_2)} - \frac{5}{3}}$$

and for temperature,

$$T = \left(\frac{\partial E}{\partial S} \right) = \frac{2}{3k(N_1 + N_2)} \frac{3\pi \hbar^2 (N_1 + N_2)^{5/3}}{m V^{2/3}} e^{\frac{2S}{3k(N_1 + N_2)} - \frac{5}{3}} = \frac{2\pi \hbar^2 (N_1 + N_2)^{2/3}}{mk V^{2/3}} e^{\frac{2S}{3k(N_1 + N_2)} - \frac{5}{3}}$$

and finally the chemical potentials

$$\mu_1 = -kT \ln \left[\frac{V}{N_1} \left(\frac{mkT}{2\pi\hbar} \right)^{3/2} \right]$$

$$\mu_2 = -kT \ln \left[\frac{V}{N_2} \left(\frac{mkT}{2\pi\hbar} \right)^{3/2} \right]$$

— **Physics 215A: Statistical Mechanics**

Problem 1

Show that the electric polarization p of a classical ideal gas consisting of N diatomic molecules having constant electric dipole moment μ is given by,

$$p = \frac{N\mu}{V} \left(\coth \left(\frac{\mu E}{kT} \right) - \frac{kT}{\mu E} \right)$$

where V is the volume of the gas and E is the external electric field. Prove that for $|\mu E| \ll kT$, the dielectric constant ε of the gas is given by,

$$\varepsilon = 1 + \frac{4\pi N\mu^2}{3VkT}$$

The induced polarization in the molecules is to be disregarded, and the electric field acting on the molecules is assumed to be equal to the external electric field.

My Solution

We consider rotational degrees of freedom to contribute to the Hamiltonian, as well as interaction potential effects from the dipole moment and the electric field:

$$H = H_{\text{rot}} + H_{\text{electric}} = \frac{P_{\theta}^2}{2I} + \frac{P_{\phi}^2 \sin^2 \theta}{2I} - \mu E \cos \theta$$

We are after the electric polarization as:

$$p = \frac{N}{V} P = \frac{N}{V} \langle \mu \cos \theta \rangle$$

$$P = \langle \mu \cos \theta \rangle = \frac{\partial \ln Z_{\text{rot}}}{\partial (\beta E)}$$

$$\begin{aligned} Z_{\text{rot}} &= \frac{1}{(2\pi\hbar)^2} \int d\theta d\phi dp_{\theta} dp_{\phi} e^{-\beta H} = \frac{1}{(2\pi\hbar)^2} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} d\theta d\phi \int dp_{\theta} dp_{\phi} e^{-\beta \left[\frac{P_{\theta}^2}{2I} + \frac{P_{\phi}^2 \sin^2 \theta}{2I} \right] + \beta \mu E \cos \theta} \\ &= (2\pi)^2 \frac{I}{\beta \hbar^2} \int_0^{2\pi} d\theta e^{\beta \mu E \cos \theta} \end{aligned}$$

change variables: $x = \cos \theta$

$$\begin{aligned} Z_{\text{rot}} &= (2\pi)^2 \frac{I}{\beta \hbar^2} \int_{-1}^1 dx e^{\beta \mu E x} = (2\pi)^2 \frac{I}{\beta \hbar^2} \left[\frac{1}{\beta \mu E} \right] \Big|_{-1}^1 = (2\pi)^2 \frac{I}{\beta \hbar^2} \left[\frac{1}{\beta \mu E} (e^{\beta \mu E} - e^{-\beta \mu E}) \right] \\ &= (2\pi)^2 \frac{I}{\beta \hbar^2} \left[\frac{2 \sinh \beta \mu E}{\beta \mu E} \right] = 8\pi^2 \frac{I}{\beta \hbar^2} \left[\frac{\sinh \beta \mu E}{\beta \mu E} \right] = \frac{8\pi^2 I}{(\beta \hbar)^2 \mu E} \sinh \beta \mu E \end{aligned}$$

$$\begin{aligned} p &= \frac{N}{V} \frac{\partial}{\partial (\beta E)} \left[\ln \left\{ \frac{8\pi^2 I}{(\beta \hbar)^2 \mu E} \sinh \beta \mu E \right\} \right] = \frac{N}{V} \frac{\partial}{\partial (\beta E)} \left[\ln \left\{ \frac{8\pi^2 I}{(\beta \hbar)^2 \mu E} \right\} + \ln \{ \sinh \beta \mu E \} \right] \\ &= \frac{N}{V} \left[-\frac{1}{\beta E} + \frac{1}{\sinh \beta \mu E} \cosh (\beta \mu E) \mu \right] = \frac{N}{V} \left[\frac{\mu}{\sinh \beta \mu E} \cosh (\beta \mu E) - \frac{1}{\beta E} \right] \end{aligned}$$

$$\boxed{p = \frac{N}{V} \mu \left[\coth \mu \beta E - \frac{1}{\beta E \mu} \right]}$$

Knowing p ,
 $p = \frac{E}{4\pi}(\epsilon - 1) \longrightarrow \epsilon = \frac{4\pi}{E}p + 1$

but first lets use the approximation given by Taylor expanding the $\coth(\beta\mu E)$:

$$\coth(\beta\mu E) \approx \frac{1}{\beta\mu E} + \frac{\beta\mu E}{3} - \frac{(\beta\mu E)^3}{45} + \dots = \frac{kT}{\mu E} + \frac{\mu E}{3kT}$$

$$\epsilon = \frac{4\pi}{E}p + 1 = \frac{4\pi}{E} \frac{N}{V} \mu \left[\frac{kT}{\mu E} + \frac{\mu E}{3kT} - \frac{kT}{E\mu} \right] + 1 = \frac{4\pi}{E} \frac{N}{V} \mu \frac{\mu E}{3kT} + 1$$

which then proves what was asked of us:

$$\epsilon = 4\pi \frac{N}{V} \frac{\mu^2}{3kT} + 1 = \boxed{\frac{4\pi\mu^2 N}{3kTV}}$$

Problem 2

Show that the energy fluctuation in a canonical distribution is given by,

$$\langle (H - E)^2 \rangle = kT^2 C_V$$

where $E = \langle H \rangle$, H is the Hamiltonian, and C_V is the specific heat at fixed volume. In a similar manner, prove the formula,

$$\langle (H - E)^3 \rangle = k^2 T^3 \left(T \left(\frac{\partial C_V}{\partial T} \right)_V + 2C_V \right)$$

Show that, in particular, for an ideal gas consisting of N monoatomic molecules (disregarding their internal structure) these equations can be reduced to,

$$\langle (H - E)^2 \rangle = \frac{2}{3N} E^2$$

$$\langle (H - E)^3 \rangle = \frac{8}{9N^2} E^3$$

My Solution

This problem really just boils down to computing a quotient rule derivative. This next equation will be crucial to the proof:

$$\langle (H - E)^2 \rangle = \langle H^2 \rangle - \langle H \rangle^2$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = -k\beta^2 \left(\frac{\partial E}{\partial \beta} \right) = -\frac{1}{kT^2} \left(\frac{\partial E}{\partial \beta} \right)$$

$$\begin{aligned} \frac{\partial E}{\partial \beta} &= \frac{\partial}{\partial \beta} \left[\frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \right] = \frac{(\sum_i E_i e^{-\beta E_i})^2 - Z \sum_i E_i^2 e^{-\beta E_i}}{Z^2} = \left(\frac{1}{Z} \sum_i E_i e^{-\beta E_i} \right)^2 - \frac{1}{Z} \sum_i E_i^2 e^{-\beta E_i} \\ &= \langle H \rangle^2 - \langle H^2 \rangle \end{aligned}$$

knowing how E changes with β , we can use this information to write C_V in terms of these expectation values:

$$C_V = -\frac{1}{kT^2} \left(\frac{\partial E}{\partial \beta} \right) = -\frac{1}{kT^2} \left[\langle H \rangle^2 - \langle H^2 \rangle \right] = \frac{1}{kT^2} \left[\langle H^2 \rangle - \langle H \rangle^2 \right]$$

Solving for $\langle H^2 \rangle - \langle H \rangle^2$:

$$\langle H^2 \rangle - \langle H \rangle^2 = kT^2 C_V$$

Hence,

$$\boxed{\langle (H - E)^2 \rangle = \langle H^2 \rangle - \langle H \rangle^2 = kT^2 C_V}$$

and knowing that for an ideal gas, $C_V = \frac{3}{2} NkT$,

$$\langle (H - E)^2 \rangle = kT^2 C_V = kT^2 \left[\frac{3}{2} NkT \right] = \frac{3}{2} N (kT)^2$$

and knowing the energy as,

$$E = \frac{3}{2} NkT \longrightarrow kT = \frac{2}{3} \frac{E}{N}$$

Simply plug this into the expectation value expression:

$$\langle (H - E)^2 \rangle = \frac{3}{2} N (kT)^2 = \frac{3}{2} N \left[\frac{2}{3} \frac{E}{N} \right]^2 = \boxed{\frac{2}{3} \frac{E^2}{N}}$$

And for the cubed formula, we compute the second derivative and make use of an earlier result:

$$\begin{aligned} \langle (H - E)^3 \rangle &= \langle H^3 \rangle - 3 \langle H^2 \rangle \langle H \rangle + 2 \langle H \rangle^3 = \frac{\partial^2 E}{\partial \beta^2} \\ \frac{\partial^2 E}{\partial \beta^2} &= -kT^2 \frac{\partial}{\partial T} \frac{\partial E}{\partial \beta} = -kT^2 \frac{\partial}{\partial T} [-kT^2 C_V] = k^2 T^2 [2TC_V + T^2 \frac{\partial C_V}{\partial T}] = k^2 T^3 [2C_V + T \frac{\partial C_V}{\partial T}] \end{aligned}$$

Therefore,

$$\boxed{\langle (H - E)^3 \rangle = k^2 T^3 \left[2C_V + T \frac{\partial C_V}{\partial T} \right]}$$

and,

$$\langle (H - E)^3 \rangle = k^2 T^3 [2C_V + T \frac{\partial C_V}{\partial T}] = \left(\frac{2}{3} \frac{E}{N} \right)^2 \left[2T \left(\frac{3}{2} N \left(\frac{2}{3} \frac{E}{N} \right)^2 \right) + \left(\frac{3}{2} N \left(\frac{2}{3} \frac{E}{N} \right) \right) \right] = \boxed{\frac{8}{9} \frac{E^3}{N^2}}$$

Problem 3

If the free volume $\bar{V}$ of a classical system is defined by,

$$\bar{V}^N = \prod_{i=1}^N \int d^3 \mathbf{q}_i e^{(\bar{U} - U(\mathbf{q}_i))/kT}$$

where $\bar{U}$ is the average potential energy of the system and $U(\mathbf{q}_i)$ is the potential energy as a function of the particle configuration, then show that the entropy is given by,

$$S = \frac{5}{2} Nk + Nk \ln \left(\frac{\bar{V}}{N\lambda^3} \right)$$

$$\lambda^2 = \frac{2\pi\hbar^2}{mkT}$$

In what sense is it justified to refer to $\bar{V}$ as the free volume of the system? Substantiate your answer by considering a particular case – for example, the case of a hard sphere gas.

My Solution

$$\begin{aligned}
Z_N(T) &= \frac{1}{h^{3N}N!} \prod_{i=1}^N \int d\mathbf{q}_i d\mathbf{p}_i e^{-\beta H(p,q)} = \frac{1}{h^{3N}N!} \prod_{i=1}^N \int d\mathbf{q}_i d\mathbf{p}_i e^{-\beta \left[\frac{\mathbf{p}_i^2}{2m} + U(\mathbf{q}_i) \right]} \\
&= \frac{1}{h^{3N}N!} \prod_{i=1}^N \int d\mathbf{q}_i d\mathbf{p}_i e^{-\beta \left[\frac{\mathbf{p}_i^2}{2m} + U(\mathbf{q}_i) \right]} e^{-\beta \bar{U}} e^{\beta \bar{U}} \\
&= \frac{1}{h^{3N}N!} \prod_{i=1}^N \int d\mathbf{q}_i d\mathbf{p}_i e^{\beta [\bar{U} - U(\mathbf{q}_i)]} e^{-\beta \left[\frac{\mathbf{p}_i^2}{2m} - \bar{U} \right]} \\
&= \frac{\bar{V}^N}{h^{3N}N!} \left[\int d\mathbf{p}_i e^{-\beta \left[\frac{\mathbf{p}_i^2}{2m} - \bar{U} \right]} \right]^N \\
&= \frac{\bar{V}^N}{h^{3N}N!} \left[\int_0^\infty dp 4\pi p^2 e^{-\beta \left[\frac{p^2}{2m} - \bar{U} \right]} \right]^N = \frac{\bar{V}^N}{h^{3N}N!} e^{N\beta \bar{U}} \int_0^\infty dp 4\pi p^2 e^{-N\beta \frac{p^2}{2m}} \\
&= \frac{\bar{V}^N}{h^{3N}N!} e^{\frac{3}{2}N} \int_0^\infty dp 4\pi p^2 e^{-N\beta \frac{p^2}{2m}} = \frac{\bar{V}^N}{h^{3N}N!} e^{\frac{3}{2}N} \left[(2\pi m k T)^{3N/2} \right] = \left(\frac{\bar{V}}{\lambda^3} \right)^N \frac{e^{\frac{3}{2}N}}{N!} \\
\\
S &= \frac{\partial}{\partial T} \left[kT \ln \left\{ \left(\frac{\bar{V}}{\lambda^3} \right)^N \frac{e^{\frac{3}{2}N}}{N!} \right\} \right] = k \frac{\partial}{\partial T} T \left[\ln \left\{ \left(\frac{\bar{V}}{\lambda^3} \right)^N \right\} + \frac{3}{2}N - N \ln \{N\} + N \right] \\
&= k \frac{\partial}{\partial T} T \left[N \ln \left\{ \frac{\bar{V}}{\lambda^3} \right\} + \frac{3}{2}N - N \ln \{N\} + N \right] \\
&= k \left[N \ln \left\{ \frac{\bar{V}}{N\lambda^3} \right\} + \frac{3}{2}N + N \right] \\
\boxed{S} &= Nk \ln \left\{ \frac{\bar{V}}{N\lambda^3} \right\} + \frac{5}{2}Nk
\end{aligned}$$

It makes sense to refer to this as the free volume since we are excluding the volume that is occupied by the other particles in the configuration, which is shown by the weighting inside the exponential as a subtraction of a term that depends on the location of the other particles. Free in the sense that its the volume that is freely available for the particles to move in.

To substantiate, in the context of a hard sphere gas, there is infinite potential at every location where there exists a particle since these tiny hard spheres are considered impenetrable. This then proves useful in this case since not all the volume is available to be traversed by each hard sphere.

Submitted by Delano Campos on .

— Physics 215A: Statistical Mechanics

1. Problem 1

N monomeric units are arranged along a straight line to form a chain molecule, or polymer (picture below). Each monomeric unit is assumed to be capable of being either in state α or in state β , as schematically depicted in the Figure below by the red and yellow colors respectively. The respective lengths and energies in these states are l_α, l_β and E_α, E_β . Derive the relation between the total length L of the chain molecule and the tension f applied between the two ends of the molecule. Use the canonical ensemble with tension f .

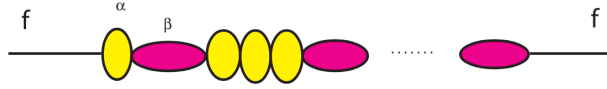


Figure 1: Linear chain of monomers α, β .

My Solution

Since this problem entails one degree of freedom in the monomers, we simply sum over available states in this degree to make the single monomer partition function, then extend to N monomers:

The key conceptual idea here is that in the context of generalized ensembles, we see these generalized conjugate variables pop up like tension and displacement which now add contributions to the Hamiltonian:

$$Z = \sum_i e^{\beta[H(p,q) - \sum_j f_j x_j(p,q)]} = e^{-\beta[E_\alpha - f_\alpha l_\alpha]} + e^{-\beta[E_\beta - f_\beta l_\beta]}$$

And really all that is left to do is realize that the partition function gives us the probabilities associated to each state, which in turn, will change the length of the monomer chain. I attempt to construct the probability of one monomer being in state α or β , and then extend to N monomers:

$$\begin{aligned} P_\alpha + P_\beta &= 1 \\ P_\alpha &= \frac{e^{-\beta[E_\alpha - f_\alpha l_\alpha]}}{\sum_i e^{-\beta[E_i - f_i l_i]}} = \frac{e^{-\beta[E_\alpha - f_\alpha l_\alpha]}}{e^{-\beta[E_\alpha - f_\alpha l_\alpha]} + e^{-\beta[E_\beta - f_\beta l_\beta]}} \\ P_\beta &= \frac{e^{-\beta[E_\beta - f_\beta l_\beta]}}{\sum_i e^{-\beta[E_i - f_i l_i]}} = \frac{e^{-\beta[E_\beta - f_\beta l_\beta]}}{e^{-\beta[E_\alpha - f_\alpha l_\alpha]} + e^{-\beta[E_\beta - f_\beta l_\beta]}} \end{aligned}$$

so attaching a probability to each state, we can compute the ensemble averages of each length:

$$\begin{aligned} \langle l_\alpha \rangle &= P_\alpha l_\alpha \\ \langle l_\beta \rangle &= P_\beta l_\beta \end{aligned}$$

and to find the total length, we check these ensemble averages by summing over all monomers:

$$\langle L \rangle = \sum_i [\langle l_\alpha \rangle_i + \langle l_\beta \rangle_i] = N[\langle l_\alpha \rangle + \langle l_\beta \rangle] = N \left[\frac{l_\alpha e^{-\beta[E_\alpha - f_\alpha l_\alpha]}}{e^{-\beta[E_\alpha - f_\alpha l_\alpha]} + e^{-\beta[E_\beta - f_\beta l_\beta]}} + \frac{l_\beta e^{-\beta[E_\beta - f_\beta l_\beta]}}{e^{-\beta[E_\alpha - f_\alpha l_\alpha]} + e^{-\beta[E_\beta - f_\beta l_\beta]}} \right]$$

$$= \left[\frac{N}{Z} \left[l_\alpha e^{-\beta[E_\alpha - f_\alpha l_\alpha]} + l_\beta e^{-\beta[E_\beta - f_\beta l_\beta]} \right] \right]$$

2. Problem 2

The potential energy of a system of charged particles, characterized by particle charge e and number density $n(\mathbf{r})$, is given by,

$$U = \frac{e^2}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + e \int d^3\mathbf{r} \phi_{\text{ext}}(\mathbf{r})n(\mathbf{r})$$

where $\phi_{\text{ext}}(\mathbf{r})$ is the potential of an external electric field. Assume that the entropy of the system, apart from an additive constant, is given by the formula,

$$S = -k \int d^3\mathbf{r} n(\mathbf{r}) \ln [n(\mathbf{r})]$$

Using these expressions, derive the equation for the number density $n(\mathbf{r})$ at equilibrium, as well as the total electric potential $\phi(\mathbf{r})$ which includes the effects of ϕ_{ext} and the potential generated by the charge density $en(\mathbf{r})$.

My Solution

The requirement here is to minimize the Helmholtz Free Energy. As such, it will require functional derivatives and a popular one called the Coulomb Energy Functional:

$$F = E - TS = U - TS$$

$$U = \frac{e^2}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + e \int d^3\mathbf{r} \phi_{\text{ext}}(\mathbf{r})n(\mathbf{r})$$

Then,

$$F = \frac{e^2}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + e \int d^3\mathbf{r} \phi_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + kT \int d^3\mathbf{r} n(\mathbf{r}) \ln [n(\mathbf{r})]$$

Naming the terms iteratively,

$$F_1 = \frac{e^2}{2} \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$F_2 = e \int d^3\mathbf{r} \phi_{\text{ext}}(\mathbf{r})n(\mathbf{r})$$

$$F_3 = kT \int d^3\mathbf{r} n(\mathbf{r}) \ln [n(\mathbf{r})]$$

Computing the functional derivative for F_1 (and all the other terms) and noticing this is just the Coulomb Potential Energy Functional, we can conclude the result quickly:

$$\frac{\delta F_1}{\delta n(\mathbf{r})} = \frac{e^2}{2} \frac{\delta}{\delta n(\mathbf{r})} \left[\int \int d^3\mathbf{r} d^3\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right] = e^2 \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

$$\frac{\delta F_2}{\delta n(\mathbf{r})} = e \frac{\delta}{\delta n(\mathbf{r})} \left[\int d^3\mathbf{r} \phi_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \right] = e\phi_{\text{ext}}(\mathbf{r})$$

$$\delta F_3 = kT \delta \left(\int d^3\mathbf{r} n(\mathbf{r}) \ln [n(\mathbf{r})] \right) = kT \int d^3\mathbf{r} \{ \delta n(\mathbf{r}) \ln [n(\mathbf{r})] + \delta(\ln [n(\mathbf{r})]) \} = kT \int d^3\mathbf{r} \delta n(\mathbf{r}) \left\{ \ln [n(\mathbf{r})] + \frac{1}{n(\mathbf{r})} \delta n(\mathbf{r})n(\mathbf{r}) \right\}$$

$$= kT \int d^3\mathbf{r} \delta n(\mathbf{r}) \{ \ln [n(\mathbf{r})] + \delta n(\mathbf{r}) \}$$

and so,

$$\frac{\delta F_3}{\delta n(\mathbf{r})} = kT \frac{1}{\delta n(\mathbf{r})} \left[\int d^3\mathbf{r} \delta n(\mathbf{r}) \{ \ln [n(\mathbf{r})] + \delta n(\mathbf{r}) \} \right] = kT [\ln [n(\mathbf{r})] + 1]$$

Putting it all together,

$$\frac{\delta F}{\delta n(\mathbf{r})} = e^2 \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + e\phi_{\text{ext}}(\mathbf{r}) + kT(\ln [n(\mathbf{r})] + 1) = 0$$

and then just solving for $n(\mathbf{r})$

$$e^2 \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + e\phi_{\text{ext}}(\mathbf{r}) + kT(\ln [n(\mathbf{r})] + 1) = 0$$

$$kT \ln [n(\mathbf{r})] = -e^2 \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - e\phi_{\text{ext}}(\mathbf{r}) - kT$$

$$\ln [n(\mathbf{r})] = -\frac{e^2}{kT} \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{e}{kT} \phi_{\text{ext}}(\mathbf{r}) - 1$$

$$\Rightarrow n(\mathbf{r}) = e^{-\frac{e^2}{kT} \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \frac{e}{kT} \phi_{\text{ext}}(\mathbf{r}) - 1} = \boxed{e^{-\frac{e^2}{kT} \phi_{\text{self}}(\mathbf{r}) - \frac{e}{kT} \phi_{\text{ext}}(\mathbf{r}) - 1}}$$

and then the total given by:

$$\phi(\mathbf{r}) = \phi_{\text{ext}}(\mathbf{r}) + \phi_{\text{self}}(\mathbf{r}) = \boxed{\phi_{\text{ext}}(\mathbf{r}) + \int d^3\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}$$

3. Problem 3

Determine the grand canonical partition function of a gaseous system of magnetic atoms (with total angular momentum $J = \frac{1}{2}$ and $g = 2$) that can have, in addition to the kinetic energy, a magnetic potential energy equal to $\mu_B H$ or $-\mu_B H$, depending on their orientation in the magnetic field H . Derive an expression for the magnetization of the system, and calculate how much heat will be given off by the system when the magnetic field is reduced from H to zero at constant volume and constant temperature.

My Solution

Grand Canonical ensemble theory is valuable, and we introduce a new variable to sum over, since now N can exchange particles with our reservoir. Since per state we need the number of particles specified, as well as the energy, we introduce a double sum in the discrete case.

We can define the generalized ensemble partition function as a sum over the Boltzmann factor with generalized conjugate variables:

$$Z = \sum_i e^{-\beta[H(p,q) - fx(p,q)]}$$

then for the case of the grand canonical partition function, its simply a subset of this above definition when $f = \mu$ and $x = N$ such that now these fluctuations in N are accounted for through a second sum. I would like to make a special mention of the normalization I am including in the grand canonical partition function with the $\frac{1}{N!}$ and NOT h^{3N} due to the non-continuity of the spin degrees of freedom considered here, since this problem is vaguely hinting at quantum statistics. I have read some literature saying that often, the over counting normalization for indistinguishably is embedded into the grand partition function definition, but I am going to explicitly leave it as a term in the front for the purposes of my learning. I have also seen this written with and without them, so I am leaving the explicit notation since we have not officially gotten to statistics that solve the over-counting problem yet, based on

Fermi-Dirac or Bose-Einstein statistics:

$$Z^{gc} = \frac{1}{N!} \sum_{N=0}^{\infty} \sum_i e^{-\beta[E_i - \mu N]} = \frac{1}{N!} \sum_N \sum_i e^{-\beta E_i} e^{\beta \mu N} = \frac{1}{N!} \sum_N Z_1^N e^{\beta \mu N} = \frac{1}{N!} \sum_N (Z_1 e^{\beta \mu})^N$$

where I am using the notation of Z_1^{gc} to denote the grand canonical ensemble to distinguish it from the canonical, or any other.

In our case,

$$Z_1 = \sum_i e^{-\beta E_i} = e^{-\beta \mu H} + e^{\beta \mu H}$$

$$Z_N = \frac{1}{N!} Z_1^N = \frac{1}{N!} (e^{-\beta \mu H} + e^{\beta \mu H})^N$$

and so the grand partition function can be written as:

$$Z^{gc} = \frac{1}{N!} \sum_N (Z_1 e^{\beta \mu})^N = \frac{1}{N!} \sum_N (e^{-\beta \mu H} + e^{\beta \mu H})^N (e^{\beta \mu})^N$$

and we can recognize a term in the sum which comes from the Nth particle partition function as a cosh :

$$\cosh(x) = \frac{1}{2}[e^x + e^{-x}] \implies (e^{-\beta \mu H} + e^{\beta \mu H})^N = 2^N \cosh^N(\beta \mu H)$$

$$Z^{gc} = \sum_N \frac{1}{N!} 2^N e^{N \beta \mu} \cosh^N(\beta \mu H) = \sum_N \frac{[2e^{\beta \mu} \cosh(\beta \mu H)]^N}{N!}$$

Which is recognized as a Taylor-Series expansion of the exponential function:

$$e^x = \sum_{N=0}^{\infty} \frac{x^N}{N!}$$

$$Z^{gc} = \sum_N \frac{[2e^{\beta \mu} \cosh(\beta \mu H)]^N}{N!} = \boxed{e^{2e^{\beta \mu} \cosh(\beta \mu H)}}$$

To find magnetization, I will derive an expression from first principles. Though I know it may not necessary and I can state it, I think it serves me best to start from the definition of the Gibbs free energy and work from there:

$$\begin{aligned} G &= F - fX = E - TS - fX = E - TS - HM \\ &= -kT \ln(Z^{gc}(\beta, H)) \end{aligned}$$

Where I am calling $M = \langle m \rangle$ as the ensemble average of the magnetization, m, and H as the magnetic field. Finding the Gibbs Free-Energy differential,

$$dG = -SdT - Xdf = -SdT - MdH$$

Next I fix the temperature and solve for M:

$$\begin{aligned} M &= -\left(\frac{\partial G}{\partial H}\right)_T = kT \frac{\partial}{\partial H} (\ln[Z^{gc}(\beta, H)]) = kT \frac{\partial}{\partial H} \left(\ln \left[e^{2e^{\beta \mu} \cosh(\beta \mu H)} \right] \right) \\ &= kT \frac{\partial}{\partial H} \left(e^{2e^{\beta \mu} \cosh(\beta \mu H)} \right) = 2\beta \mu e^{\beta \mu} kT \sinh(\beta \mu H) e^{2e^{\beta \mu} \cosh(\beta \mu H)} = \boxed{2\mu e^{\beta \mu} \sinh(\beta \mu H) e^{2e^{\beta \mu} \cosh(\beta \mu H)}} \end{aligned}$$

Knowing that any change in energy will leave as heat:

$$dE = Q = T \Delta S$$

and knowing that

$$M = -\left(\frac{\partial G}{\partial H}\right) \text{ and } S = -\left(\frac{\partial G}{\partial T}\right)$$

$$MdH = SdT \implies S = M \frac{\partial H}{\partial T}$$

Differentiating in H:

$$\frac{dS}{dH} = \frac{d}{dH} \left[M \frac{\partial H}{\partial T} \right] = \frac{\partial M}{\partial H} \frac{\partial H}{\partial T} + M \frac{\partial}{\partial H} \frac{\partial H}{\partial T} = \frac{\partial M}{\partial T}$$

$$\Delta S = \int dS = \int_H^0 \left(\frac{\partial M}{\partial T} \right)_H dH$$

where I then ask for forgiveness for my abuse of notation with the differentials. Next step requires a triple product rule in T, then integration over H from H to 0, but the physics is already done here and I do not think its worthwhile to compute this manually. I leave the integral and show the heat in terms of it since **the question does not specify the final form of the heat:**

$$\Delta S = \int_H^0 \frac{\partial}{\partial T} \left[2\mu e^{\beta\mu} \sinh(\beta\mu H) e^{2e^{\beta\mu} \cosh(\beta\mu H)} \right] dH$$

$$\Rightarrow Q = T\Delta S = \boxed{T \int_H^0 \frac{\partial}{\partial T} \left[2\mu e^{\beta\mu} \sinh(\beta\mu H) e^{2e^{\beta\mu} \cosh(\beta\mu H)} \right] dH}$$

— Physics 215A: Statistical Mechanics

1. Problem 1

For any two density matrices ρ and ρ' which are operators in the same Hilbert space $\mathcal{H}$ the following inequality holds

$$S(\rho) = -k\text{Tr}(\rho \ln \rho) \leq -k\text{Tr}(\rho \ln \rho')$$

with equality being attained if and only if $\rho' = \rho$. Prove this famous result. [Hint: express ρ and ρ' in their respective orthonormal bases (which will in general be different from one another), and use the property that the function $f(x) = x - 1 - \ln x$ satisfies $f(x) > 0$ for all $x > 0$ except for $x = 1$ where it vanishes.].

My Solution

First, I show in general that:

$$S(\rho) = -k\text{Tr}[\rho \ln(\rho)] = -k \sum_i p_i \ln(p_i)$$

$$\begin{aligned} -k\text{Tr}[\rho \ln(\rho)] &= -k\text{Tr}[(\sum_i p_i |\phi_i\rangle \langle \phi_i|) \ln(\sum_i p_i |\phi_i\rangle \langle \phi_i|)] = -k\text{Tr}[\sum_i p_i (|\phi_i\rangle \langle \phi_i|) \ln(p_i |\phi_i\rangle \langle \phi_i|)] \\ &= -k \sum_i p_i \ln(p_i) \text{Tr}[|\phi_i\rangle \langle \phi_i|] \\ &= -k \sum_i p_i \ln(p_i) \end{aligned}$$

Knowing this, I similarly compute the right side of the inequality in terms its orthonormal basis,
 $-k\text{Tr}(\rho \ln \rho') = -k \sum_i p_i \ln(p'_i)$

Next I make use of the relative entropy and use Wikipedia's notation:

$$\begin{aligned} D(\rho||\rho') &= \text{Tr}[\rho(\ln(\rho) - \ln(\rho'))] = \text{Tr}[\rho \ln(\rho) - \rho \ln(\rho')] = k \sum_i p_i \ln(p_i) - k \sum_i p_i \ln(p'_i) \\ &= k \sum_i p_i (\ln(p_i) - \ln(p'_i)) = k \sum_i p_i \ln \frac{p_i}{p'_i} \end{aligned}$$

Then I make use of the hint, $f(x) = x - 1 - \ln x \geq 0$ where in our case $x \Rightarrow \frac{p_i}{p'_i}$

$$\begin{aligned} k \sum_i p_i \ln \frac{p_i}{p'_i} &= k \sum_i p_i \left(\frac{p_i}{p'_i} - 1 - \ln \frac{p_i}{p'_i} \right) \geq 0 \\ &= k \sum_i \frac{p_i^2}{p'_i} - k \sum_i p_i + k \sum_i p_i \ln \frac{p'_i}{p_i} \geq 0 \end{aligned}$$

Using, $\sum_i p_i = \sum_i p'_i = 1$

$$= k \sum_i p_i \ln \frac{p'_i}{p_i} = k \sum_i p_i [\ln p'_i - \ln p_i] \geq 0$$

$$= k \sum_i p_i \ln p'_i \geq k \sum_i p_i \ln p_i \implies \boxed{-k\text{Tr}(\rho \ln \rho') \geq -k\text{Tr}(\rho \ln \rho)}$$

2. Problem 2

Let $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$ be the Hilbert space of a system composed of two subsystems A, B with respective Hilbert spaces $\mathcal{H}_A$ and $\mathcal{H}_B$. Let ρ be a density matrix of the full system and let $\rho_A = \text{Tr}_{\mathcal{H}_B}(\rho)$ and $\rho_B = \text{Tr}_{\mathcal{H}_A}(\rho)$ be the reduced density matrices of the subsystems. Using the result of Problem 1, prove the property of *sub-additivity* of the entropy, which may be stated as follows.

$$S(\rho) \leq S(\rho_A) + S(\rho_B)$$

My Solution

For this problem I use some properties of the partial trace without proof. The proof for the property is generally not nice since I wanted to try to prove it before I made use of it .

I start this problem with the relative entropy used in the last problem, keeping consistent notation:

$$\begin{aligned} D(\rho || (\rho_A \otimes \rho_B)) &= \text{Tr}[\rho(\ln(\rho) - \ln(\rho_A \otimes \rho_B))] \\ &= \text{Tr}[\rho \ln(\rho) - \rho \ln(\rho_A \otimes \rho_B)] \\ &= \text{Tr}[\rho \ln(\rho)] - \text{Tr}[\rho \ln(\rho_A \otimes \rho_B)] \end{aligned}$$

Where I then call on the implication of problem 1:

$$D(\rho || (\rho_A \otimes \rho_B)) \text{ implies } -k\text{Tr}(\rho \ln(\rho_A \otimes \rho_B)) \geq -k\text{Tr}(\rho \ln \rho)$$

Next I think the steps that follow become obvious. We use partial trace properties to split the left hand side of the inequality and recover the desired result.

$$\begin{aligned} -k\text{Tr}(\rho \ln(\rho_A \otimes \rho_B)) &= -k\text{Tr}[\rho \ln(\rho_A) \otimes I_B + I_A \otimes \ln(\rho_B)] \\ &= -k\text{Tr}[\rho \ln(\rho_A) \otimes I_B] - k\text{Tr}[I_A \otimes \ln(\rho_B)] \\ &= -k\text{Tr}[\rho_A \ln(\rho_A)] - k\text{Tr}[\rho_B \ln(\rho_B)] \end{aligned}$$

All together,

$$\begin{aligned} -k\text{Tr}[\rho_A \ln(\rho_A)] - k\text{Tr}[\rho_B \ln(\rho_B)] &\geq -k\text{Tr}(\rho \ln \rho) \\ \boxed{= S(\rho) \leq S(\rho_A) + S(\rho_B)} \end{aligned}$$

3. Problem 3

Consider a system with Hamiltonian $H = H_0 + \lambda H_1$, and denote the un-normalized density matrix $\rho_0(\beta) = e^{-\beta H_0}$ with $T = 1/k\beta$.

- (a) Prove that the (un-normalized) density matrix $\rho(\beta)$ for H satisfies the integral equation,

$$\rho(\beta) = \rho_0(\beta) - \lambda \rho_0(\beta) \int_0^\beta d\beta' e^{\beta' H_0} H_1 \rho(\beta')$$

- (b) Obtain the correction to ρ_0 and the partition function to second order in λ .

My Solution

- (a) Recalling that when dealing with time dependent perturbation theory in 221B, we could re-write the Schrodinger equation in integral form and express the time evolution operator as an iterative series. The solution to the perturbation problem goes as,

$$i\hbar \frac{\partial U(t_0, t)}{\partial t} = H(t_0, t)U(t_0, t) = (H_0 + \lambda H_1)U(t_0, t)$$

where,

$$H(t_0, t) = e^{\frac{i}{\hbar} H_0(t-t_0)} H_1 e^{-\frac{i}{\hbar} H_0(t-t_0)}$$

The time evolution operator is re written in integral form as

$$U(t_0, t) = 1 - \frac{i}{\hbar} \int dt' H(t_0, t)U(t_0, t)$$

I only illustrated the above to remind ourselves of the Dyson series and re-writing exponential operators in integral form. I will write our current form of the exponential operator in integral form and the problem is simple. To first order,

$$\rho(\beta) = e^{-\beta(H_0 + \lambda H_1)} \approx e^{-\beta' H_0} \left(1 - \int e^{-\beta' H_0} \lambda H_1 e^{-\beta' H} d\beta' \right)$$

and then since $\rho_0(\beta) = e^{-\beta' H_0}$,

$$\rho(\beta) = \rho_0(\beta) \left(1 - \int \rho(\beta') \lambda H_1 e^{-\beta' H_0} d\beta' \right) = \boxed{\rho_0(\beta) - \rho_0(\beta) \int \rho(\beta') \lambda H_1 e^{-\beta' H_0} d\beta'}$$

$$\begin{aligned} \text{(b)} \quad \rho(\beta) &= \rho_0(\beta) + \lambda \rho_1(\beta) + \lambda^2 \rho_2(\beta) \\ &= \rho_0(\beta) - \rho_0(\beta) \int \rho(\beta') \lambda H_1 e^{-\beta' H_0} d\beta' \\ &= \rho_0(\beta) - \rho_0(\beta) \int e^{-\beta' H_0} \lambda H_1 [\rho_0(\beta') + \lambda \rho_1(\beta') + \lambda^2 \rho_2(\beta')] d\beta' \\ &= \rho_0(\beta) - \lambda \rho_0(\beta) \int e^{-\beta' H_0} H_1 \rho_0(\beta') d\beta' - \lambda^2 \rho_0(\beta) \int e^{-\beta' H_0} H_1 \rho_1(\beta') d\beta' - \lambda^3 \rho_0(\beta) \int e^{-\beta' H_0} H_1 \rho_2(\beta') d\beta' \end{aligned}$$

Coefficient by coefficient:

$$\begin{aligned} \rho_0(\beta) &= \rho_0(\beta) \\ \rho_1(\beta) &= -\rho_0(\beta) \int e^{-\beta' H_0} H_1 \rho_0(\beta') d\beta' \\ \rho_2(\beta) &= -\rho_0(\beta) \int e^{-\beta' H_0} H_1 \rho_1(\beta') d\beta' = -\rho_0(\beta) \int e^{-\beta' H_0} H_1 \left[-\rho_0(\beta') \int e^{-\beta'' H_0} H_1 \rho_0(\beta'') d\beta'' \right] d\beta' \\ &= \rho_0(\beta) \int H_1^2 \rho_0(\beta') e^{-\beta' H_0} d\beta' \left[\int e^{-\beta'' H_0} \rho_0(\beta'') d\beta'' \right] \end{aligned}$$

And the partition function given by,

$$\begin{aligned} Z(\beta) &= \text{Tr}[\rho(\beta)] = \text{Tr}[\rho_0(\beta) + \lambda \rho_1(\beta) + \lambda^2 \rho_2(\beta)] \\ &= \text{Tr}[\rho_0(\beta)] + \lambda \text{Tr}[\rho_1(\beta)] + \lambda^2 \text{Tr}[\rho_2(\beta)] \\ &= \text{Tr}[\rho_0(\beta)] - \lambda \text{Tr} \left[\rho_0(\beta) \int e^{-\beta' H_0} H_1 \rho_0(\beta') d\beta' \right] + \lambda^2 \text{Tr} \left[\rho_0(\beta) \int H_1^2 \rho_0(\beta') e^{-\beta' H_0} d\beta' \int e^{-\beta'' H_0} \rho_0(\beta'') d\beta'' \right] \end{aligned}$$

4. Problem 4

Let again $\mathcal{H} = \mathcal{H}_A \otimes \mathcal{H}_B$ be the total Hilbert space of a system composed of two subsystems A, B . Consider a normalized pure state $|\psi\rangle \in \mathcal{H}$, and denote by $\rho_A = \text{Tr}_{\mathcal{H}_B}(|\psi\rangle\langle\psi|)$ and $\rho_B = \text{Tr}_{\mathcal{H}_A}(|\psi\rangle\langle\psi|)$ the corresponding reduced density matrices.

- (a) Prove the *Schmidt purification theorem* which states that there exist orthonormal bases $|A, i\rangle$ and $|B, j\rangle$ of $\mathcal{H}_A$ and $\mathcal{H}_B$ respectively such that the reduced density matrices ρ_A and ρ_B are both diagonal, and the pure state $|\psi\rangle$ may be expressed as follows,

$$|\psi\rangle = \sum_i \sqrt{p_i} |A, i\rangle \otimes |B, i\rangle$$

- (b) Use the result of (a) to show that the ranks of ρ_A and ρ_B are equal.
(c) Use the result of (a) to show that the entropies are equal $S(\rho_A) = S(\rho_B) = -k \sum_i p_i \ln p_i$.
[Hint: Take the basis $|A, i\rangle$ such that ρ_A is diagonal in this basis, with eigenvalues p_i .]

My Solution

- (a.) I first compute ρ_A and ρ_B explicitly from knowing how $|\psi\rangle$ is defined in the Schmidt purification theorem, and show that both ρ_A and ρ_B are diagonal in their respective orthonormal bases $|A, i\rangle$ and $|B, j\rangle$.

$$\begin{aligned} \rho_A &= \text{Tr}_{\mathcal{H}_B}[|\psi\rangle\langle\psi|] \\ &= \text{Tr}_{\mathcal{H}_B}\left[\left(\sum_i \sqrt{p_i} |A, i\rangle \otimes |B, i\rangle\right)\left(\sum_j \sqrt{p_j} \langle A, j| \otimes \langle B, j| \right)\right] \\ &= \text{Tr}_{\mathcal{H}_B}\left[\sum_i \sum_j \sqrt{p_i} \sqrt{p_j} (|A, i\rangle \otimes |B, i\rangle \langle A, j| \otimes \langle B, j|)\right] \\ &= \text{Tr}_{\mathcal{H}_B}\left[\sum_i \sum_j \sqrt{p_i p_j} (|A, i\rangle \langle A, j| \otimes |B, i\rangle \langle B, j|)\right] \\ &= \sum_i \sum_j \sqrt{p_i p_j} |A, i\rangle \langle A, j| \text{Tr}_{\mathcal{H}_B}[|B, i\rangle \langle B, j|] \\ &= \sum_{ij} \sqrt{p_i p_j} |A, i\rangle \langle A, j| \delta_{ij} \\ &= \sum_i \sqrt{p_i^2} |A, i\rangle \langle A, i| \\ &= \boxed{\sum_i p_i |A, i\rangle \langle A, i|} \end{aligned}$$

Likewise, we can compute ρ_B ,

$$\begin{aligned} \rho_B &= \text{Tr}_{\mathcal{H}_A}[|\psi\rangle\langle\psi|] \\ &= \text{Tr}_{\mathcal{H}_A}\left[\left(\sum_i \sqrt{p_i} |A, i\rangle \otimes |B, i\rangle\right)\left(\sum_j \sqrt{p_j} \langle A, j| \otimes \langle B, j| \right)\right] \\ &= \text{Tr}_{\mathcal{H}_A}\left[\sum_i \sum_j \sqrt{p_i} \sqrt{p_j} (|A, i\rangle \otimes |B, i\rangle \langle A, j| \otimes \langle B, j|)\right] \\ &= \text{Tr}_{\mathcal{H}_A}\left[\sum_i \sum_j \sqrt{p_i p_j} (|A, i\rangle \langle A, j| \otimes |B, i\rangle \langle B, j|)\right] \\ &= \sum_i \sum_j \sqrt{p_i p_j} |B, i\rangle \langle B, j| \text{Tr}_{\mathcal{H}_A}[|A, i\rangle \langle A, j|] \\ &= \sum_{ij} \sqrt{p_i p_j} |B, i\rangle \langle B, j| \delta_{ij} \\ &= \sum_i \sqrt{p_i^2} |B, i\rangle \langle B, i| \\ &= \boxed{\sum_i p_i |B, i\rangle \langle B, i|} \end{aligned}$$

Which shows that from the definition of the expression of a pure state $|\psi\rangle$, we can find ρ_A and ρ_B as diagonal matrices in their respective bases $|A, i\rangle$ and $|B, j\rangle$, each with identical eigenvalues as the next

- (b.) This part was essentially solved by part a after one simple observation about the identical eigenvalues. Since rank tells us the amount of non-zero eigenvalues, and both ρ_A and ρ_B both share identical eigenvalues, I can then claim that any non-zero eigenvalue in ρ_A will also be reflected in ρ_B , and vice-versa.

Therefore, since the eigenvalues of ρ_A and ρ_B are identical, the ranks must also be as well.

(c.) We know in general that the Von Neumann entropy can be expressed as

$$S(\rho) = -k\text{Tr}[\rho \ln \rho] = -k \sum_i p_i \ln(p_i)$$

Where ρ is some density matrix and p_i are the eigenvalues of the density matrix. Since from part a we found that

$$\begin{aligned}\rho_A &= \sum_i p_i |A, i\rangle \langle A, i| \\ \rho_B &= \sum_i p_i |B, i\rangle \langle B, i|\end{aligned}$$

Then we can conclude the Von Neumann entropy's of each as

$$\begin{aligned}S(\rho_A) &= -k\text{Tr}[\rho_A \ln \rho_A] = -k \sum_i p_i \ln(p_i) \\ S(\rho_B) &= -k\text{Tr}[\rho_B \ln \rho_B] = -k \sum_i p_i \ln(p_i)\end{aligned}$$

Which shows that $S(\rho_A) = S(\rho_B) = -k \sum_i p_i \ln(p_i)$ by the argument presented in part a.

— Physics 215A: Statistical Mechanics

Problem 1

For a gas of interacting particles obeying the van der Waals equation of state,

$$\left(P + \frac{aN^2}{V^2}\right)(V - bN) = NkT \quad (0-1)$$

(a) Show that we have the following relation between specific heat functions,

$$C_P - C_V = Nk \left(1 - \frac{2aN(V - bN)^2}{kTV^3}\right)^{-1} \quad (0-2)$$

(b) Show that with constant specific heat C_V , an adiabatic thermodynamic transformation proceeds according to the following equation,

$$(V/N - b)T^{C_V/Nk} = \text{constant} \quad (0-3)$$

(c) Further show that the temperature change resulting from an expansion of the gas (into vacuum) from volume V_1 to volume V_2 is given by,

$$T_2 - T_1 = \frac{N^2a}{C_V} \left(\frac{1}{V_2} - \frac{1}{V_1}\right) \quad (0-4)$$

My Solution

$$\begin{aligned} \text{(a)} \quad dH &= dE + PdV + VdP \\ &= \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV + VdP = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV = C_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV \end{aligned}$$

Then since $dE = TdS - PdV \implies TdS = dE + PdV$

$$\begin{aligned} TdS &= C_P dT = C_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV \\ C_P &= C_V + \left(\frac{\partial E}{\partial T}\right)_T \frac{\partial V}{\partial T} + P \frac{\partial V}{\partial T} \end{aligned}$$

Using maxwell relation: $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$

$$C_P - C_V = -T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Computing each,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial}{\partial T} \left[\frac{NkT}{V - bN} - \frac{aN^2}{V^2} \right] = \frac{Nk}{V - bN}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{PbNV^3}{NkV^3 + aN^2(V - bN)}$$

Which comes from differentiating the given van der waals equation of state and using the chain rule.

$$C_P - C_V = -T \left[\frac{Nk}{V - bN} \right] \left[\frac{PbNV^3}{NkV^3 + aN^2(V - bN)} \right] = Nk \left(1 - \frac{2aN(V - bN)^2}{kTV^3} \right)^{-1}$$

(b) $dE = dTC_V = TdS - PdV = 0$

$$\begin{aligned}
C_V dT + PdV &= 0 \\
C_V dT + \left[\frac{NkT}{V-bN} - \frac{aN^2}{V^2} \right] dV &= 0 \\
\int \frac{C_V}{T} dT &= - \int \frac{Nk}{V-bN} dV \\
C_V \ln(T) &= -Nk \ln(V-bN) + c_1 \\
\ln(T^{C_V}) &= \ln \left((V-bN)^{-Nk} + c_1 \right) \\
T^{C_V} &= (V-bN)^{-Nk} + c_1 \\
\boxed{(V/N-b)T^{C_V/Nk} &= \text{constant}}
\end{aligned}$$

(c) $\Delta E = E_2 - E_1 = C_V \Delta T = 0$

From part a,
 $E = -\frac{aN^2}{V} + F_0 - F'_0 T = C_V T - \frac{aN^2}{V}$

Back into the first equation of part c,
 $\Delta E = E_2 - E_1 = C_V \Delta T - \left[\frac{aN^2}{V_2} - \frac{aN^2}{V_1} \right] = 0$
 $\Delta T + \frac{1}{C_V} \left[-\frac{aN^2}{V_2} + \frac{aN^2}{V_1} \right] = 0$
 $\boxed{T_2 - T_1 = \frac{aN^2}{C_V} \left[\frac{1}{V_2} - \frac{1}{V_1} \right]}$

Problem 2

The proper formalism for implementing Fermi-Dirac and Bose-Einstein statistics for interacting particles is quantum field theory. The purpose of this problem is to show that the formalism of quantum field theory does reproduce the partition function and occupation numbers for free systems, studied already previously with other methods. We shall assume that the spectrum of one-particle states is known, and given by a set of discrete energy levels ϵ_i . For free particles in a box, one may think of the index i as the composite index of the momentum quantum numbers $i = (n_x, n_y, n_z)$ combined with any additional internal quantum numbers, but we shall keep the discussion general.

Now, for each value of the index i , we introduce a pair of oscillators,

$$\begin{array}{llll}
\text{Fermi-Dirac} & b_i, b_i^\dagger & \{b_i, b_j\} = 0, & \{b_i, b_j^\dagger\} = \delta_{ij} \\
\text{Bose-Einstein} & a_i, a_i^\dagger & [a_i, a_j] = 0, & [a_i, a_j^\dagger] = \delta_{ij}
\end{array} \quad (0.1)$$

where $\{, \}$ stands for the anti-commutator, $[,]$ stands for the commutator, and δ_{ij} is the Kronecker delta. The Hamiltonians and particle number operators are defined as follows,

$$\begin{array}{llll}
\text{Fermi-Dirac} & H_{FD} = \sum_i \epsilon_i b_i^\dagger b_i & N_{FD} = \sum_i b_i^\dagger b_i \\
\text{Bose-Einstein} & H_{BE} = \sum_i \epsilon_i a_i^\dagger a_i & N_{BE} = \sum_i a_i^\dagger a_i
\end{array} \quad (0.2)$$

The ground state $|0\rangle$ is defined by $b_i|0\rangle = 0$ for FD and $a_i|0\rangle = 0$ for BE, both for all i .

(a) Show that the following states are eigenstates of the Hamiltonian and the particle number operators and evaluate their energy and particle number,

$$\begin{array}{ll}
\text{Fermi-Dirac} & b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_N}^\dagger |0\rangle \\
\text{Bose-Einstein} & a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_N}^\dagger |0\rangle
\end{array} \tag{0.3}$$

- (b) What is the interpretation of the states with particle number equal to 1, 2, etc?
(c) Determine the quantum permutation symmetry properties under an arbitrary permutation of particles for both the FD and BE cases.
(d) Calculate the partition function and the occupation numbers for both cases.
(e) Compare with our earlier results.

My Solution

$$\begin{aligned}
\text{(a)} \quad H_{FD} b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_N}^\dagger |0\rangle &= \sum_i \epsilon_i b_i^\dagger b_i b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_N}^\dagger |0\rangle \\
&= \boxed{(\epsilon_{i_1} + \epsilon_{i_2} + \cdots \epsilon_{i_N}) b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_N}^\dagger |0\rangle}
\end{aligned}$$

Which shows that the state was an eigenfunction of the hamiltonian with eigenvalue $\epsilon_{i_1} + \epsilon_{i_2} + \cdots \epsilon_{i_N}$

$$\begin{aligned}
&\text{likewise,} \\
N_{FD} b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_N}^\dagger |0\rangle &= \sum_i b_i^\dagger b_i b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_N}^\dagger |0\rangle \\
&= \left(b_{i_1}^\dagger b_{i_1} + b_{i_2}^\dagger b_{i_2} \cdots b_{i_N}^\dagger b_{i_N} \right) b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_N}^\dagger |0\rangle \\
&= (N_1 + N_2 \cdots N_N) b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_N}^\dagger |0\rangle \\
&= \boxed{N b_{i_1}^\dagger b_{i_2}^\dagger \cdots b_{i_N}^\dagger |0\rangle}
\end{aligned}$$

which is again an eigenfunction of the hamiltonian with eigenvalue N.

$$\begin{aligned}
H_{BE} a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_N}^\dagger |0\rangle &= \sum_i \epsilon_i a_i^\dagger a_i a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_N}^\dagger |0\rangle \\
&= \boxed{(\epsilon_{i_1} + \epsilon_{i_2} + \cdots \epsilon_{i_N}) a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_N}^\dagger |0\rangle}
\end{aligned}$$

$$\begin{aligned}
N_{FD} a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_N}^\dagger |0\rangle &= \sum_i a_i^\dagger a_i a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_N}^\dagger |0\rangle \\
&= \left(a_{i_1}^\dagger a_{i_1} + a_{i_2}^\dagger a_{i_2} \cdots a_{i_N}^\dagger a_{i_N} \right) a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_N}^\dagger |0\rangle \\
&= (N_1 + N_2 \cdots N_N) a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_N}^\dagger |0\rangle \\
&= \boxed{N a_{i_1}^\dagger a_{i_2}^\dagger \cdots a_{i_N}^\dagger |0\rangle}
\end{aligned}$$

- (b) The particle number on each state represents different particles in particular states of i or j. In FD statistics, we know there is a cap on the number of particles in a single state i or j, while in BE statistics, this does not hold.

In general the interpretation is that for FD, then $i \neq j$ since no two particles can be in the same state, but for BE, we can have $i = j$. One creation operator acting on the ground state represents some particle in a specific state either i or j, and a condition on the number of allowed particles comes from whether the particle is a fermion or boson.

- (c) Under an arbitrary permutation of particles for FD, the problem statement really provides us enough to understand the symmetry properties by looking at the commutation properties of each case.

Given that,
 $\{b_i, b_j\} = 0$

$$\{b_i, b_j^\dagger\} = \delta_{ij}$$

This implies antisymmetry since when you exchange two different creation operators on independent particles, you pick up a negative sign. In general, these are anti-symmetric

Using similar logic for the bose-einstein case and using,

$$\begin{aligned} [a_i, a_j] &= 0 \\ [a_i, a_j^\dagger] &= \delta_{ij} \end{aligned}$$

We see these guys commute and thus can be understood that their permutations are symmetric

$$(d) \quad Z = \text{Tr} \left[e^{-\beta(\hat{H} - \mu \hat{N})} \right] = \text{Tr} \left[e^{-\beta \sum_i (\epsilon_i - \mu) b_i^\dagger b_i} \right]$$

Then we let the trace operate on individual degrees of freedom:

$$\begin{aligned} Z &= \prod_i \text{Tr}_i \left[e^{-\beta \sum_i (\epsilon_i - \mu) b_i^\dagger b_i} \right] = \prod_i \sum_{i=0,1} \langle n_i | e^{-\beta(\epsilon_i - \mu) b_i^\dagger b_i} | n_i \rangle = \prod_i \sum_{i=0,1} e^{-\beta(\epsilon_i - \mu) n_i} \\ &= \prod_i (1 + e^{-\beta(\epsilon_i - \mu)}) \end{aligned}$$

Therefore for FD,

$$\boxed{Z = \prod_i \left[1 + e^{-\beta(\epsilon_i - \mu)} \right]}$$

Likewise for BE,

$$Z = \text{Tr} \left[e^{-\beta(\hat{H} - \mu \hat{N})} \right] = \text{Tr} \left[e^{-\beta \sum_i (\epsilon_i - \mu) a_i^\dagger a_i} \right]$$

$$\begin{aligned} Z &= \prod_i \text{Tr}_i \left[e^{-\beta \sum_i (\epsilon_i - \mu) a_i^\dagger a_i} \right] = \prod_i \sum_{i=0}^{\infty} \langle n_i | e^{-\beta(\epsilon_i - \mu) a_i^\dagger a_i} | n_i \rangle = \prod_i \sum_{i=0}^{\infty} e^{-\beta(\epsilon_i - \mu) n_i} \\ &= \prod_i \left[\frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}} \right] \end{aligned}$$

Therefore for BE,

$$\boxed{Z = \prod_i \left[\frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}} \right]}$$

For the occupation numbers,

$$\langle n_i \rangle_{FD} = \frac{1}{Z_{FD}} \text{Tr} \left[b_i^\dagger b_i e^{-\beta(H - \mu N)} \right] = \frac{e^{-\beta(\epsilon_i - \mu)}}{1 + e^{-\beta(\epsilon_i - \mu)}} = \boxed{\frac{1}{1 + e^{-\beta(\epsilon_i - \mu)}}}$$

Likewise,

$$\langle n_i \rangle_{BE} = \frac{1}{Z_{BE}} \text{Tr} \left[a_i^\dagger a_i e^{-\beta(H - \mu N)} \right] = \frac{e^{-\beta(\epsilon_i - \mu)}}{1 - e^{-\beta(\epsilon_i - \mu)}} = \boxed{\frac{1}{e^{-\beta(\epsilon_i - \mu)} - 1}}$$

(e) Compared to the partition functions we obtained earlier, these match to what we expected.

For fermi-dirac statistics, we obtained a partition function that is identical to the methods using the grand canonical ensemble from earlier. Same with the occupation number for FD.

The BE partition function also reflects the same result we obtained while using the grand canonical ensemble methods. In conjunction with the partition function, we also observe an identical occupation number.

$$\boxed{\text{all results are identical.}}$$

Submitted by Delano Campos on .

— Physics 215A: Statistical Mechanics: **Systems of Fermions**

Problem 1

- (a) Derive a formula for the specific heat C_V of a system of electrons at arbitrary temperature T and chemical potential μ in terms of the FD occupation number

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1} \quad \beta = \frac{1}{kT}$$

and the density of states $D(\varepsilon)$ for one electron per unit volume at energy ε .

- (b) Derive a formula for C_V to leading non-zero order for strong degeneracy for general $D(\varepsilon)$.
(c) Derive a formula for C_V to leading non-zero order for weak degeneracy for general $D(\varepsilon)$.
(d) Apply these formulas to a system of free non-relativistic electrons. Do you recover the standard high T result for C_V ? Explain.

My Solution

- (a) Since we are after the specific heat which is defined as,

$$C_V = \frac{\partial E}{\partial T},$$

First looking at the energy in the discrete case, I will then extend to the continuous case:

$$E = \sum_i G_i n_i \epsilon_i = \sum_i \frac{G_i \epsilon_i}{1 + e^{\beta(\epsilon_i - \mu)}}$$

Where G_i is the number of states in the coarse graining cell, and n_i is the number of particles per state defined as,

$$n_i = \frac{1}{1 + e^{\beta(\epsilon_i - \mu)}}$$

for Fermi-Dirac statistics. Extending the discrete case to the continuous case, we must introduce a density function to which we can integrate over to exchange the sum for an integral. I include this as the density of states $D(\epsilon)$,

$$E/V = \int_0^\infty \epsilon f(\epsilon) D(\epsilon) d\epsilon$$

$$C_V = \frac{\partial E}{\partial T} = C_V = \frac{\partial}{\partial T} \left[V \int_0^\infty \epsilon f(\epsilon) D(\epsilon) d\epsilon \right] = V \int_0^\infty \epsilon \frac{\partial f(\epsilon)}{\partial T} D(\epsilon) d\epsilon = V \int_0^\infty \epsilon D(\epsilon) \frac{\partial}{\partial T} \left[\frac{1}{1 + e^{\beta(\epsilon - \mu)}} \right] d\epsilon$$

Computing the derivative,

$$\frac{\partial f(\epsilon)}{\partial T} = \frac{\partial f(\epsilon)}{\partial \beta} \frac{\partial \beta}{\partial T} = \left[\frac{-(\epsilon - \mu) e^{\beta(\epsilon - \mu)}}{[e^{\beta(\epsilon - \mu)} + 1]^2} \right] \left[\frac{-1}{kT^2} \right] = \frac{(\epsilon - \mu) e^{\beta(\epsilon - \mu)}}{kT^2 [e^{\beta(\epsilon - \mu)} + 1]^2}$$

$$C_V = V \int_0^\infty \epsilon D(\epsilon) \frac{(\epsilon - \mu) e^{\beta(\epsilon - \mu)}}{kT^2 [e^{\beta(\epsilon - \mu)} + 1]^2} d\epsilon = \boxed{\frac{V}{kT^2} \int_0^\infty \epsilon D(\epsilon) \frac{(\epsilon - \mu) e^{\beta(\epsilon - \mu)}}{[e^{\beta(\epsilon - \mu)} + 1]^2} d\epsilon}$$

- (b) In the strong degeneracy regime, we know that the temperature of the system is much smaller than the Fermi Temperature, T_F . Since most fermions occupy states with energy near the Fermi Energy E_F , the statistics are dominated by the energies close to the Fermi Energy. A direct consequence of the high degeneracy limit is that the occupation probability approaches 1 for energies under the chemical potential and is null for energies above it since, $\epsilon \approx \mu$. I adjust C_V knowing that the integrand is dominated for energies around the chemical potential:

$$\text{w } C_V = \frac{V}{kT^2} \int_0^\infty \epsilon D(\epsilon) \frac{(\epsilon-\mu)e^{\beta(\epsilon-\mu)}}{[e^{\beta(\epsilon-\mu)}+1]^2} d\epsilon = \frac{V}{kT^2} \int_{-\infty}^\infty D(\mu) \frac{(\epsilon-\mu)^2 e^{\beta(\epsilon-\mu)}}{[e^{\beta(\epsilon-\mu)}+1]^2} d\epsilon = \frac{V}{kT^2} D(\mu) \int_{-\infty}^\infty \frac{(\epsilon-\mu)^2 e^{\beta(\epsilon-\mu)}}{[e^{\beta(\epsilon-\mu)}+1]^2} d\epsilon$$

Since,

$$e^{\beta(\epsilon-\mu)} = e^{\beta(\epsilon-\mu)/2} e^{\beta(\epsilon-\mu)/2}$$

and

$$1 = e^{\beta(\epsilon-\mu)/2} e^{-\beta(\epsilon-\mu)/2},$$

Then we can rewrite the denominator in the integrand as:

$$\frac{1}{[e^{\beta(\epsilon-\mu)}+1]^2} = \frac{1}{[e^{\beta(\epsilon-\mu)/2} e^{\beta(\epsilon-\mu)/2} + e^{\beta(\epsilon-\mu)/2} e^{-\beta(\epsilon-\mu)/2}]^2} = \frac{1}{e^{\beta(\epsilon-\mu)} [e^{\beta(\epsilon-\mu)/2} + e^{-\beta(\epsilon-\mu)/2}]^2}$$

We then get cancellation from a term in the numerator,

$$C_V = \frac{V}{kT^2} D(\mu) \int_{-\infty}^\infty \frac{(\epsilon-\mu)^2 e^{\beta(\epsilon-\mu)}}{e^{\beta(\epsilon-\mu)} [e^{\beta(\epsilon-\mu)/2} + e^{-\beta(\epsilon-\mu)/2}]^2} d\epsilon = \frac{V}{kT^2} D(\mu) \int_{-\infty}^\infty \frac{(\epsilon-\mu)^2}{[e^{\beta(\epsilon-\mu)/2} + e^{-\beta(\epsilon-\mu)/2}]^2} d\epsilon$$

a change of variables $x = \epsilon - \mu$

$$= \frac{V}{kT^2} D(\mu) \int_{-\infty}^\infty \frac{x^2}{[e^{\beta x/2} + e^{-\beta x/2}]^2} d\epsilon = \frac{V}{4kT^2} D(\mu) \int_{-\infty}^\infty \frac{x^2}{\cosh^2(\beta x/2)} dx$$

Another change of variables, $u = \beta x/2$

$$C_V = \frac{V}{4kT^2} D(\mu) \int_{-\infty}^\infty \frac{8u^2/\beta^2}{\cosh^2 u} \frac{du}{\beta} = 2VD(\mu)k^2T \int_{-\infty}^\infty \frac{u^2}{\cosh^2 u} du = 2VD(\mu)kT^2 \left[\frac{\pi^2}{6} \right] = \boxed{\frac{\pi^2}{3} VD(\mu)k^2T}$$

$$\begin{aligned} \text{(c) } C_V &= V \int_0^\infty \epsilon \frac{\partial f(\epsilon)}{\partial T} D(\epsilon) d\epsilon = V \int_0^\infty \epsilon \frac{\partial}{\partial T} [e^{-\beta(\epsilon-\mu)}] D(\epsilon) d\epsilon = V \int_0^\infty \epsilon \left[\frac{(\epsilon-\mu)}{kT^2} \right] [e^{-\beta(\epsilon-\mu)}] D(\epsilon) d\epsilon \\ &= \frac{V}{kT^2} \int_0^\infty \epsilon(\epsilon-\mu) e^{-\beta(\epsilon-\mu)} D(\epsilon) d\epsilon \end{aligned}$$

and without the specific form of the density of states, we cannot simplify this integral expression any further as we were able to do in the part above. Therefore the specific heat is given by,

$$\boxed{C_V = \frac{V}{kT^2} \int_0^\infty \epsilon(\epsilon-\mu) e^{-\beta(\epsilon-\mu)} D(\epsilon) d\epsilon}$$

- (d) Since for free-non relativistic electrons,

$$D(\epsilon) = 4\pi V(2m)^{3/2} \sqrt{\epsilon}/h^3$$

Then we can find the weak degeneracy case,

$$\begin{aligned} C_V &= \frac{V}{kT^2} \int_0^\infty \epsilon(\epsilon-\mu) e^{-\beta(\epsilon-\mu)} \left[4\pi V(2m)^{3/2} \sqrt{\epsilon}/h^3 \right] d\epsilon = \frac{V}{kT^2} \int_0^\infty \epsilon(\epsilon-\mu) e^{-\beta(\epsilon-\mu)} \left[4\pi V(2m)^{3/2} \sqrt{\epsilon}/h^3 \right] d\epsilon \\ &= \frac{4\pi V^2}{kT^2} (2m)^{3/2}/h^3 \int_0^\infty \epsilon^{3/2}(\epsilon-\mu) e^{-\beta(\epsilon-\mu)} d\epsilon \end{aligned}$$

Letting mathematica integrate,

$$= \frac{4\pi V^2}{kT^2} (2m)^{3/2} / h^3 \left[\frac{3e^{\beta\mu} \sqrt{\pi}}{8\beta^{7/2}} (5 - 2\beta\mu) \right] = \frac{(2\pi m)^{3/2} V^2}{Th^3 \beta^{5/2}} \left[\frac{15}{4} - \frac{3}{2} \beta\mu \right]$$

$$\frac{C_V}{Nk} = \frac{\frac{(2\pi m)^{3/2} V^2}{Th^3 \beta^{5/2}} \left[\frac{15}{4} - \frac{3}{2} \beta\mu \right]}{4\pi V^2 (2m)^{3/2} / h^3 \int_{-\infty}^{\infty} \epsilon^{1/2} e^{-\beta(\epsilon-\mu)} d\epsilon} = \left[\frac{15}{4} - \frac{3}{2} \beta\mu \right]$$

The standard result does not appear, since we did not compute the specific heat for fixed number of particles N , instead this was for constant μ . I did this problem probably 6 times and I still do not clearly see how to recover the usual result, though I know we should get it.

Problem 2

We evaluate the electric current density of electrons which is produced by heating up a metal in the presence of an external electric potential. The potential energy for electrons inside the metal vanishes, while just outside the metal it is $W > 0$. The electrons are otherwise non-interacting, and filled up to chemical potential μ with $\mu < W$. We consider the problem at sufficiently low temperature so that μ may be identified with the Fermi energy.

- State the condition on its momentum for an electron to be able to escape from the metal to the outside, as a function of W and μ ;
- Derive a general expression for the current density I of electrons leaving the metal;
- Obtain an approximation of your result in (b) valid for sufficiently low temperatures.

My Solution

$$(a) \quad \frac{p^2}{2m} > W \implies \boxed{p > \sqrt{2mW}}$$

- The current density is generally defined as,

$$\mathbf{J} = \rho \mathbf{v} = \rho \mathbf{p} / m \implies J = ep / m$$

and in our case, I will make use of the density of states and integrate over momentum space since there is a distribution of states available. As such, I need to restrict the bounds of integration to the only meaningful values of the momentum, which are the ones above in the threshold given by a. Each momentum state has a different weighting given by their occupation number.

$$\begin{aligned} J &= \frac{e}{m} \int p f(p) D(p) = \frac{e}{m} \int p \left[\frac{1}{1 + e^{\beta(p^2/2m - \mu)}} \right] \left[2 \frac{d^3 p}{(2\pi\hbar)^3} \right] = \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \int p \left[\frac{1}{1 + e^{\beta(p^2/2m - \mu)}} \right] d^3 p \\ &= \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \int p \left[\frac{d^3 p}{1 + e^{\beta(p^2/2m - \mu)}} \right] = \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \int p_z dp_x dp_y dp_z \left[\frac{1}{1 + e^{\beta(p^2/2m - \mu)}} \right] \\ &= \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \int \int \int \left[\frac{p_z dp_x dp_y dp_z}{1 + e^{\beta((p_x^2 + p_y^2 + p_z^2)/2m - \mu)}} \right] \\ &= \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{\sqrt{2m(W-\mu)}}^{\infty} \left[\frac{p_z dp_z}{1 + e^{\beta((p_x^2 + p_y^2 + p_z^2)/2m - \mu)}} \right] \end{aligned}$$

Which is quite the integral. Therefore, the general expression for the current density is given by,

$$\boxed{J = \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{\sqrt{2mW}}^{\infty} \left[\frac{p_z dp_z}{1 + e^{\beta((p_x^2 + p_y^2 + p_z^2)/2m - \mu)}} \right]}$$

(c) For low temperatures,

$$f(\epsilon) = \frac{1}{1+e^{\beta(\epsilon-\mu)}} \approx e^{-\beta(\epsilon-\mu)} = e^{-\beta(p^2/2m-\mu)}$$

$$\begin{aligned} J &= \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \int p_z \left[e^{-\beta(p^2/2m-\mu)} \right] d^3p = \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \int p_z \left[e^{-\beta[(p_x^2+p_y^2+p_z^2)/2m-\mu]} \right] dp_x dp_y dp_z \\ &= \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{\sqrt{2mW}}^{\infty} e^{-\beta[(p_x^2+p_y^2+p_z^2)/2m-\mu]} p_z dp_z \end{aligned}$$

I carry out this integration in mathematica, which produces the following result,

$$J = \frac{2e}{m} \frac{1}{(2\pi\hbar)^3} \left[\frac{2m^2\pi}{\beta^2} e^{\beta(\mu-W)} \right] = \frac{4em}{\beta^2} \frac{\pi}{8\pi^3\hbar^3} e^{\beta(\mu-W)} = \frac{em}{\beta^2 2\pi^2\hbar^3} e^{\beta(\mu-W)} = \boxed{\frac{em(kT)^2}{2\pi^2\hbar^3} e^{\beta(\mu-W)}}$$

Submitted by Delano Campos on 5/24/24.

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— Physics 215A: Statistical Mechanics: **Bose-Einstein Statistics and Strange Stars**

Problem 1

Atoms in a solid vibrate about their respective equilibrium positions with small oscillations. Debye approximated the normal vibrations with the elastic vibrations of an isotropic body and assumed that the number of vibrational modes $g(\omega)d\omega$ having angular frequency between ω and $\omega + d\omega$ is given by,

$$g(\omega) = 9N \frac{\omega^2}{\omega_D^3} \theta(\omega_D - \omega) \quad (0.1)$$

Here, θ is the Heaviside step function, defined by $\theta(x) = 0$ for $x < 0$ and $\theta(x) = 1$ for $x > 0$, N is the number of atoms, and ω_D is the Debye frequency.

- (a) Explain the choice of the normalization factor $9N$ in the function $g(\omega)$ given above.
- (b) Derive the formulas in terms of $g(\omega)$ for the free energy F and the internal energy E .
- (c) Calculate the specific heat at constant volume C_V of a solid with the Debye model.
- (d) Determine the temperature dependence of C_V at high as well as at low temperatures.

My Solution

- (a) The factor of 9 in front of the ensures proper normalization for the number of degrees of freedom for each particle. In a lattice of atoms which can vibrate, there are three translational degrees of freedom for every direction of vibration which is possible. I integrate across all vibrational modes with general normalization constant A , and show this must be 9:

$$\begin{aligned} 3N &= \int_0^{\omega_D} g(\omega) d\omega = \int_0^{\omega_D} AN \frac{\omega^2}{\omega_D^3} \theta(\omega_D - \omega) d\omega \\ 3 &= A/\omega_D^3 \int_0^{\omega_D} \omega^2 d\omega \\ 3 &= \frac{A}{\omega_D^3} \left[\frac{1}{3} \omega_D^3 \right] = \frac{A}{3} \\ \boxed{A} &= 9 \end{aligned}$$

- (b) $F = -kT \ln \{Z\}$

$$Z = \sum_n e^{-\beta(n+\frac{1}{2})\hbar\omega_i} = \sum_n e^{-\beta n\hbar\omega_i} e^{-\beta \frac{\hbar\omega_i}{2}}$$

Which we recognize as a geometric series with a known result of the sum:

$$\sum_{n=0}^{\infty} ax^n = \frac{a}{1-x}$$

For our case, $a = e^{-\beta \frac{\hbar\omega_i}{2}}$ and $x = e^{-\beta \hbar\omega_i}$:

$$Z = \prod_i \frac{e^{-\beta \frac{\hbar\omega_i}{2}}}{1 - e^{-\beta \hbar\omega_i}} = \prod_i \frac{e^{-\beta \frac{\hbar\omega_i}{2}}}{e^{-\beta \frac{\hbar\omega_i}{2}} (e^{\beta \frac{\hbar\omega_i}{2}} - e^{-\beta \frac{\hbar\omega_i}{2}})} = \prod_i \frac{1}{e^{\beta \frac{\hbar\omega_i}{2}} - e^{-\beta \frac{\hbar\omega_i}{2}}} = \prod_i \frac{1}{2 \sinh [\beta \hbar\omega_i / 2]}$$

$$F = -kT \ln \{Z\} = F = -kT \ln \left\{ \prod_i \frac{1}{2 \sinh [\beta \hbar \omega_i / 2]} \right\}$$

exploiting how the natural log behaves under products of its argument, we can simply change the argument of products into a sum which we extract out:

$$F = -kT \sum_i \ln \left\{ \frac{1}{2 \sinh [\beta \hbar \omega_i / 2]} \right\} = kT \sum_i [\ln \{ \sinh [\beta \hbar \omega_i / 2] \} - \ln \{ \frac{1}{2} \}] = kT \sum_i \ln \{ 2 \sinh [\beta \hbar \omega_i / 2] \}$$

We now make use of the problem statement since they provided us the density of modes, and in our expression for F, we are indeed summing over frequency modes. We change the sum for an integral courtesy of $g(\omega)$.

$$\begin{aligned} F &= kT \sum_i \ln \{ 2 \sinh [\beta \hbar \omega_i / 2] \} = kT \int_0^\infty 9N \frac{\omega^2}{\omega_D^3} \theta(\omega_D - \omega) \ln \{ 2 \sinh [\beta \hbar \omega / 2] \} d\omega \\ &= \frac{9NkT}{\omega_D^3} \int_0^\infty \omega^2 \theta(\omega_D - \omega) \ln \{ 2 \sinh [\beta \hbar \omega / 2] \} d\omega = \frac{9NkT}{\omega_D^3} \int_0^{\omega_D} \omega^2 \ln \{ 2 \sinh [\beta \hbar \omega / 2] \} d\omega \\ &= \frac{9NkT}{\omega_D^3} \int_0^{\omega_D} \omega^2 \left[\frac{\beta}{2} \hbar \omega + \ln \{ 1 - e^{-\beta \hbar \omega} \} \right] d\omega \\ &= \frac{9NkT}{\omega_D^3} \int_0^{\omega_D} \omega^2 \ln \{ 1 - e^{-\beta \hbar \omega} \} d\omega \\ &= \frac{9NkT}{\omega_D^3} \int_0^{\omega_D} \omega^2 \left[- \sum_n \frac{e^{-n\beta \hbar \omega}}{n} \right] d\omega = - \frac{9NkT}{\omega_D^3} \sum_n \frac{1}{n} \int_0^{\omega_D} \omega^2 e^{-n\beta \hbar \omega} d\omega \end{aligned}$$

Which is beginning to look like a Gamma function integral. Lets change variables to use the Gamma functions properly. Let $-t = n\beta \hbar \omega$, $\frac{-dt}{n\beta \hbar} = d\omega$:

$$\begin{aligned} F &= \frac{-9NkT}{\omega_D^3} \sum_n \frac{1}{n} \int_0^{\frac{t_D}{n\beta \hbar}} \left(\frac{-t}{n\beta \hbar} \right)^2 e^{-t} \left(\frac{-dt}{n\beta \hbar} \right) = \frac{9NkT}{(\beta \hbar \omega_D)^3} \sum_n \frac{1}{n^4} \int_0^{\frac{t_D}{n\beta \hbar}} t^2 e^{-t} dt \\ &= \frac{9NkT}{(\beta \hbar \omega_D)^3} \sum_n \frac{1}{n^4} \Gamma(3) = \frac{18NkT}{(\beta \hbar \omega_D)^3} \sum_n \frac{1}{n^4} \\ &= \frac{18NkT}{(\beta \hbar \omega_D)^3} \zeta(4) = \frac{18NkT}{(\beta \hbar \omega_D)^3} \frac{\pi^4}{90} = \boxed{\frac{1}{5} \frac{N(kT\pi)^4}{(\hbar \omega_D)^3}} \\ E &= - \frac{\partial}{\partial \beta} \ln \{Z\} = \frac{-9N}{(\hbar \omega_D)^3} \frac{\partial}{\partial \beta} \left[\frac{1}{\beta^3} \sum_n \frac{1}{n^4} \int_0^{t_D/n\beta \hbar} t^2 e^{-t} dt \right] \\ &= \frac{-9N}{(\hbar \omega_D)^3} \zeta(4) \Gamma(3) \frac{\partial}{\partial \beta} \left[\frac{1}{\beta^3} \right] = \frac{27N}{(\hbar \omega_D)^3} \frac{\pi^4}{45} (kT)^4 = \boxed{\frac{3}{5} \frac{N(kT\pi)^4}{(\hbar \omega_D)^3}} \end{aligned}$$

(c,d) Since part b I decided to do alot of simplification, I am combining part c and d into one:

For low T,

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} \left[\frac{3}{5} \frac{N(kT\pi)^4}{(\hbar \omega_D)^3} \right] = \frac{12}{5} \frac{N(k\pi)^4}{(\hbar \omega_D)^3} T^3 = \frac{12}{5} \frac{Nk\pi^4 k^3}{(\hbar \omega_D)^3} T^3$$

Where I am going to define the Debye temperature as: $T_D = \frac{\hbar \omega_D}{k}$

$$\boxed{C_{V,low} = \frac{12}{5} Nk\pi^4 \left(\frac{T}{T_D} \right)^3}$$

For large T, I adjust previous expressions I had for E, and instead C_V now becomes:

$$C_V = \frac{\hbar^2}{kT^2} \int_0^\infty g(\omega) \omega^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} d\omega = \frac{9Nk(\beta \hbar)^2}{\omega_D^3} \int_0^{\omega_D} \omega^4 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2} d\omega$$

Let $x = \beta \hbar \omega$, $\omega = \frac{x}{\beta \hbar}$, $d\omega = \frac{dx}{\beta \hbar}$:

$$\begin{aligned}
&= \frac{9Nk(\beta\hbar)^2}{\omega_D^3} \int_0^{T_D/T} \left(\frac{x}{\beta\hbar}\right)^4 \frac{e^x}{(e^x-1)^2} \frac{dx}{\beta\hbar} = \frac{9Nk}{(\beta\hbar)^3 \omega_D^3} \int_0^{T_D/T} x^4 \frac{e^x}{(e^x-1)^2} dx \\
&= 9Nk \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} x^4 \frac{e^x}{(e^x-1)^2} dx \\
&\approx 9Nk \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} x^2 dx \\
&= 9Nk \left(\frac{T}{T_D}\right)^3 \left[\frac{1}{3} \left(\frac{T_D}{T}\right)^3\right]
\end{aligned}$$

$$\boxed{C_{V,high} = 3Nk}$$

Problem 2

We consider an ideal non-relativistic Bose-Einstein gas whose constituents have mass m and no internal degrees of freedom. Total particle number N , condensate particle number N_0 , T , E , V , μ and fugacity $z = e^{\beta\mu}$, are related as follows,

$$N - N_0 = \frac{V}{\lambda^3} g_{3/2}(z) \quad E = \frac{3kTV}{2\lambda^3} g_{5/2}(z) \quad (0.2)$$

As usual, we set $\lambda^2 = 2\pi\hbar^2/(mkT)$.

We now consider instead the BE gas confined to a vertical cylinder of height L in the presence of a uniform gravitational acceleration g .

- Calculate the critical temperature T_c at which BE condensation sets in under the assumption that the gravitational effects are weak, namely $mgL \ll kT_c$. Express your answer in terms m , g , L and the critical temperature T_c^0 for BE condensation in the absence of gravity.
- Show that the effect of gravity produces a discontinuity in the specific heat C_V at the BE transition T_c , and that the value of this discontinuity is given by,

$$\Delta C_V \Big|_{T_c} = -\frac{9}{8\sqrt{\pi}} \zeta\left(\frac{3}{2}\right) Nk \left(\frac{mgL}{kT_c^0}\right)^{1/2} \quad (0.3)$$

where $\zeta(x)$ is the Riemann zeta-function.

My Solution

- In class we did effectively this exact problem except for the case of a free Bose-Einstein gas where the hamiltonian is purely kinetic. In this case, only two things change from that example, the integration bounds for a term which defines the number density, and the hamiltonian in the denominator that is attached to a turn multiplying the fugacity. The gravitational potential energy of the gas now shows up in addition to kinetic energy:

$$\frac{N}{V} = \frac{1}{V} \frac{1}{z^{-1}-1} + \int_0^L \int_0^\infty \frac{d^3\mathbf{p}}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\mathbf{p}^2/2m+mg l-\mu)}-1} dl$$

Where of course our first term which shows up on the right hand side of the equality is the number of particles in the ground state:

$$N_0 = \frac{1}{z^{-1}-1}$$

Since we care about the critical temperature, we must check to see when z tends to 1, then N_0 should give back a macroscopic number of particles in the ground state and thus allows for BE condensation.

$$N - N_0 = \frac{V}{L} \int_0^L \int_0^\infty \frac{d^3\mathbf{p}}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\mathbf{p}^2/2m+mg l-\mu)}-1} dl = \frac{V}{L} \int_0^L \int_0^\infty \frac{4\pi p^2 dp}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\mathbf{p}^2/2m+mg l-\mu)}-1} dl$$

Then we change variables, $l = L\alpha$, $dl = Ld\alpha$, and also change variables with $\epsilon = p^2/2m$, $dp = \frac{m}{p}d\epsilon$:

$$\begin{aligned}
N - N_0 &= \frac{V}{L} \int_0^1 \int_0^\infty \frac{4\pi(2m\epsilon)(\sqrt{\frac{m}{2\epsilon}}d\epsilon)}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\epsilon+mgL\alpha-\mu)}-1} Ld\alpha \\
&= V \int_0^1 \int_0^\infty \frac{4\pi(2m\epsilon)(\sqrt{\frac{m}{2\epsilon}}d\epsilon)}{(2\pi\hbar)^3} \frac{1}{e^{\beta(\epsilon+mgL\alpha-\mu)}-1} d\alpha \\
&= \frac{V}{\lambda^3} \int_0^1 \int_0^\infty \frac{\epsilon^{1/2}}{e^{\beta\epsilon}e^{\beta(mgL\alpha-\mu)}-1} d\epsilon d\alpha \\
&= \frac{V}{\lambda^3} \int_0^1 \int_0^\infty \frac{\epsilon^{1/2}}{e^{\beta\epsilon}z'-1} d\epsilon d\alpha
\end{aligned}$$

Where I am calling $z' = e^{\beta(\mu-mgL\alpha)} = ze^{-\beta mgL\alpha}$. This then look like a polylog, with $\nu = 3/2$, and $z \rightarrow z'$

$$N - N_0 = \frac{V}{\lambda^3} \int_0^1 g_{\frac{3}{2}}(z') d\alpha = \frac{V}{\lambda^3} \int_0^1 g_{\frac{3}{2}}(ze^{-\beta mgL\alpha}) d\alpha$$

We then look at two cases, one in the presence of gravity and the other in the absence of gravity. Starting with $g = 0$, $z = 1$:

$$N - N_0 = \frac{V}{\lambda_0^3} \int_0^1 g_{\frac{3}{2}}(z = 1) d\alpha = \frac{V}{\lambda_0^3} \int_0^1 \zeta\left(\frac{3}{2}\right) d\alpha = \frac{V}{\lambda_0^3} \zeta\left(\frac{3}{2}\right)$$

Now the presence of gravity forces us to invoke the approximation given in the problem statement:

$$N - N_0 = \frac{V}{\lambda^3} \int_0^1 g_{\frac{3}{2}}(e^{-\beta mgL\alpha}) d\alpha \approx \frac{V}{\lambda^3} \int_0^1 g_{\frac{3}{2}}(1 - \beta mgL\alpha) d\alpha$$

We then expand the polylog around $z = 1$ knowing that $mgL\alpha \ll kT \rightarrow \beta mgL\alpha \ll 1$, we are effectively taking values extremely close to its argument. I split it into a power series and expand from there:

$$\begin{aligned}
g_{\frac{3}{2}}(z) &= \sum_{n=1}^{\infty} \frac{z^n}{n^{3/2}} \\
g_{\frac{3}{2}}(z - \delta) &= \sum_{n=1}^{\infty} \frac{(z-\delta)^n}{n^{3/2}} \approx \sum_{n=1}^{\infty} \frac{1}{n^{3/2}} (1 - n\delta + \frac{1}{2}n(n-1)\delta^2) = \sum_{n=1}^{\infty} \left[\frac{1}{n^{3/2}} - \frac{n\delta}{n^{3/2}} + \frac{n(n-1)\delta^2}{2n^{3/2}} \right] \\
&= \sum_{n=1}^{\infty} \frac{1}{n^{3/2}} - \delta \sum_{n=1}^{\infty} \frac{1}{n^{1/2}} + \frac{\delta^2}{2} \sum_{n=1}^{\infty} \frac{n-1}{n^{1/2}}
\end{aligned}$$

Where we notice a Reimann-Zeta function in the first term evaluated at $3/2$, and another in the second term at $1/2$. Negating the higher order third term:

$$g_{\frac{3}{2}}(z - \delta) = \sum_{n=1}^{\infty} \left[\frac{1}{n^{3/2}} - \frac{\delta}{n^{1/2}} \right] = \zeta\left(\frac{3}{2}\right) - \sqrt{2\pi}\delta^{1/2} = \zeta\left(\frac{3}{2}\right) - \sqrt{2\pi}(\beta mgL\alpha)^{1/2}$$

Now we have enough to work out the integrals and wrap up the solution:

$$\begin{aligned}
N - N_0 &\approx \frac{V}{\lambda^3} \int_0^1 \left[\zeta\left(\frac{3}{2}\right) - \sqrt{2\pi}(\beta mgL\alpha)^{1/2} \right] d\alpha = \frac{V}{\lambda^3} \int_0^1 \left[\zeta\left(\frac{3}{2}\right) - \sqrt{2\pi}(\beta mgL\alpha)^{1/2} \right] d\alpha \\
&= \frac{V}{\lambda^3} \int_0^1 \left[\zeta\left(\frac{3}{2}\right) - 2\sqrt{\pi}(\beta mgL\alpha)^{1/2} \right] d\alpha \\
&= \frac{V}{\lambda^3} \left[\zeta\left(\frac{3}{2}\right) - \frac{8}{3}\sqrt{\pi} \left(\frac{mgL}{kT} \right)^{1/2} \right]
\end{aligned}$$

Setting this expression equal to one we obtained earlier for no gravity,

$$\frac{V}{\lambda_0^3} \zeta\left(\frac{3}{2}\right) = \frac{V}{\lambda^3} \left[\zeta\left(\frac{3}{2}\right) - \frac{8}{3}\sqrt{\pi} \left(\frac{mgL}{kT} \right)^{1/2} \right]$$

$$\left(\frac{mkT_c^0}{2\pi\hbar}\right)^{3/2} = \left(\frac{mkT_c}{2\pi\hbar}\right)^{3/2} \left[1 - \frac{8\sqrt{\pi}}{3\zeta(\frac{3}{2})} \left(\frac{mgL}{kT_c^0}\right)^{1/2}\right]$$

$$(T_c^0)^{3/2} = T_c^{3/2} \left[1 - \frac{8\sqrt{\pi}}{3\zeta(\frac{3}{2})} \left(\frac{mgL}{kT_c^0}\right)^{1/2}\right]$$

Finally,

$$T_c = T_c^0 \left[1 - \frac{8\sqrt{\pi}}{3\zeta(\frac{3}{2})} \left(\frac{mgL}{kT_c^0}\right)^{1/2}\right]^{-2/3}$$

- (b) This portion of the problem is now pretty cool. We distinguish between the gas and matter phases and evaluate the specific heats at each of these points. A key point is the value of the fugacity changes in each phase, since in the matter phase, there is a macroscopic number of particles in the ground state since this phase of matter occurs at temperatures lower than the critical. Likewise, the inverse is true for the gas phase, $z \neq 1$ since this is above the critical temperature.

Starting with the gaseous phase by expanding:

$$g_{5/2}(ze^{-\beta mgL\alpha}) \approx g_{5/2}(z(1 - \beta mgL\alpha)) \approx g_{5/2}(1 + (z - 1) - z\beta mgL\alpha) = g_{5/2}(z)$$

$$E = \frac{3kTV}{2\lambda^3} g_{5/2}(z)$$

$$C_V = \frac{\partial E}{\partial T} = \frac{3kV}{2} \frac{\partial}{\partial T} \left[\frac{T}{\lambda^3} g_{5/2}(z) \right] = \frac{3kV}{2} \left[\frac{5}{2} \frac{1}{\lambda^3} g_{5/2}(z) + \frac{1}{\lambda^3} g_{3/2}(z) \frac{\partial z}{\partial T} \right]$$

We need to obtain the derivative from knowing N:

$$N = \frac{V}{\lambda^3} \int_0^1 d\alpha g_{3/2}(ze^{-\beta mgL\alpha})$$

$$C_V = \frac{3kV}{2} \left[\frac{5}{2} \frac{1}{\lambda^3} g_{5/2}(z) + \frac{1}{\lambda^3} g_{3/2}(z) \frac{3}{2\sqrt{\pi}} \left(\frac{\lambda}{\lambda_0}\right)^3 \left(\frac{mgL}{kT_0}\right)^{1/2} \zeta\left(\frac{3}{2}\right) \right]$$

$$= \frac{3kV}{2} \left[\frac{5}{2} \frac{1}{\lambda^3} g_{5/2}(z) + g_{3/2}(z) \frac{3}{4\sqrt{\pi}} \left(\frac{1}{\lambda_0}\right)^3 \left(\frac{mgL}{kT_0}\right)^{1/2} \zeta\left(\frac{3}{2}\right) \right]$$

$$\frac{C_{V,\text{gas}}}{Nk} = \frac{15}{4} \left(\frac{\lambda_0}{\lambda}\right)^3 \frac{g_{5/2}}{g_{3/2}} + \frac{9}{8\sqrt{\pi}} \zeta\left(\frac{3}{2}\right) \left(\frac{mgL}{kT_C^0}\right)^{1/2}$$

Now for the matter phase which is much simpler since $z = 1$:

$$E = \frac{3kTV}{2\lambda^3} \int_0^1 d\alpha g_{5/2}(z') = \frac{3kTV}{2\lambda^3} \int_0^1 d\alpha g_{5/2}(e^{-\beta mgL\alpha})$$

$$= \frac{3kTV}{2\lambda^3} \zeta\left(\frac{5}{2}\right) \int_0^1 d\alpha$$

$$= \frac{3kTV}{2\lambda^3} \zeta\left(\frac{5}{2}\right)$$

$$C_V = \frac{\partial E}{\partial T} = \frac{15}{4} \left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2} \zeta\left(\frac{5}{2}\right) kV = \frac{15}{4} \frac{kV}{\lambda^3} \zeta\left(\frac{5}{2}\right)$$

$$\frac{C_{V,\text{matter}}}{Nk} = \frac{\frac{15}{4} \frac{kV}{\lambda^3} \zeta\left(\frac{5}{2}\right)}{\frac{V}{\lambda_0^3} \zeta\left(\frac{3}{2}\right) k} = \frac{15}{4} \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \left(\frac{\lambda_0}{\lambda}\right)^3$$

Finding the difference,

$$\Delta C_V / Nk = \frac{C_{V,\text{matter}}}{Nk} - \frac{C_{V,\text{gas}}}{Nk} = \frac{15}{4} \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \left(\frac{\lambda_0}{\lambda}\right)^3 - \left[\frac{15}{4} \left(\frac{\lambda_0}{\lambda}\right)^3 \frac{g_{5/2}}{g_{3/2}} + \frac{9}{8\sqrt{\pi}} \zeta\left(\frac{3}{2}\right) \left(\frac{mgL}{kT_C^0}\right)^{1/2} \right]$$

$$= -\frac{9}{8\sqrt{\pi}} \zeta\left(\frac{3}{2}\right) \left(\frac{mgL}{kT_C^0}\right)^{1/2}$$

Therefore finally,

$$\Delta C_V = -\frac{9}{8\sqrt{\pi}} \zeta\left(\frac{3}{2}\right) N k \left(\frac{mgL}{kT_C^0}\right)^{1/2}$$

Problem 3

A “strange star” is made up of three types of quarks, the up, the down, and the strange quark, whose electric charges are respectively $+2e/3$, $-e/3$ and $-e/3$. The existence of such stars has not been verified experimentally, but has been suggested theoretically. We shall assume that the masses of the up and down are equal to $m \approx 5$ MeV, while the mass of the strange is $m_s = 100$ MeV. We shall assume that a strange star contains no electrons or any other particles, and that its total electric charge is zero so that the number of up quarks equals the sum of the number of down and strange quarks. The quarks are subject to gravity, but you may neglect electromagnetic interactions. Weak interactions may convert down quarks into strange quarks and vice-versa while emitting or absorbing energy, so that the number of up quarks is conserved and equal to N , and the sum of the number of down and strange quarks is conserved as well and also equal to N . (Weak interactions will also convert quarks into electrons, muons, tau’s and their associated neutrinos, but we shall neglect all such effects here.)

- Given that the mass of the strange quark is 20 times larger than that of the down quark, one might think that, in equilibrium, a strange star is devoid of strange quarks. Why is this argument false?
- In the limit of zero temperature, compute the fractions of down and strange quarks.
- Compute the Chandrasekhar limit of such strange stars.

My Solution

- Though one may initially think to assume that the star will want to eliminate strange quarks due to a much heavier mass and having a significant chunk of these large mass particles would be less energetically favorable, in equilibrium there is contribution from more than just energies associated to the mass.

In particular, we have seen that in fermi-dirac statistics, we get some extra pressure from degeneracy which wants to spread the fermions into neighboring states, thus not allowing optimal energy levels for minimization. We also get contribution from the fact that the strange plays a role in ensuring the charge is net neutral, and without the presence of half of the amount of up quarks available, the strange star would be electrically charged and not optimize the minimum amount of energy for equilibrium.

$$(b) \quad \frac{2}{3}N_u - \frac{1}{3}N_s - \frac{1}{3}N_d = 0 \longrightarrow 2N_u = N_s + N_d$$

$$\begin{aligned} N_u + N_s + N_d &= N \\ N_u + 2N_u &= N \\ N_u &= \frac{1}{3}N \end{aligned}$$

$$\begin{aligned} \frac{1}{3}N + N_s + N_d &= N \\ N_s + N_d &= \frac{2}{3}N \end{aligned}$$

Since we know that we are in equilibrium, $\mu_s = \mu_d$, which is also equal to the Fermi Energy for the strange and down quarks. We make use of the Fermi Momentum setting $c = \hbar = 1$

$$E_{F,s} = \mu_s = \sqrt{(p_{F,s})^2 + m_s^2} = \sqrt{3\pi^2 \frac{N_s}{V} + m_s^2}$$

$$E_{F,d} = \mu_d = \sqrt{(p_{F,d})^2 + m_d^2} = \sqrt{3\pi^2 \frac{N_d}{V} + m_d^2}$$

For large enough Fermi Momenta, we approximate the fermi momenta as being proportional to one another, modulo some ratio of the respective masses.

$$p_F^2 = \frac{N}{V} 3\pi^2 \hbar^3 = 3\pi^2 n$$

Taking ratios,

$$n_s = \frac{p_{F,s}^3}{3\pi^2}$$

$$n_d = \frac{p_{F,d}^3}{3\pi^2}$$

$$n_d/n_s = \frac{p_{F,d}^3}{p_{F,s}^3} = \frac{(p_{F,s}(m_s/m_d))^3}{p_{F,s}^3} = \left(\frac{m_s}{m_d}\right)^3 = \left(\frac{100 \text{ MeV}}{5 \text{ MeV}}\right)^3 = 8000$$

$$N_s + 8000N_s = \frac{2}{3}N$$

$$8001N_s = \frac{2}{3}N$$

$$\boxed{N_s = 0.000083N}$$

$$0.000083N + N_d = \frac{2}{3}N$$

$$\boxed{N_d = 0.6665833N}$$

Which is funny since we just argued in part a why the amount of strange quarks would not be 0.

(c) I am going to average the 3 quark masses to plug into the Chandrasekhar limit:

$$M_{\text{avg}} = \frac{1}{3}[110 \text{ MeV}] \approx 36.66 \text{ MeV}$$

$$M_c = \frac{9}{64M_{\text{avg}}^2} \left(\frac{\hbar c}{G}\right)^{3/2} = \frac{9}{64(36.66 \text{ MeV})^2} \left(\frac{(6.63 \cdot 10^{-34} \text{ J s})(3 \cdot 10^8 \text{ m/s})}{6.67 \cdot 10^{-11} \text{ Nm}^2/\text{kg}^2}\right)^{3/2}$$

$$\approx 5.2570013456 \cdot 10^{33} \text{ kg}$$

Knowing, $M_{\text{sun}} = 2 \cdot 10^{30} \text{ kg}$,

$$\frac{M_c}{M_{\text{sun}}} = \frac{5.2570013456 \cdot 10^{33} \text{ kg}}{2 \cdot 10^{30} \text{ kg}} = 2600$$

$$\boxed{M_c = 2600M_s}$$

Submitted by Delano Campos on 20 de julio de 2026.