Solutions to Problem Set #10

Problem 1: Two Identical Particles

a)

Fermions:	$|1,1,0>$	ϵ_2	$T=0$ state
	$|1,0,1>$	ϵ_3	
	$|0,1,1>$	$\epsilon_2 + \epsilon_3$	

b)

Bosons:	$|2,0,0>$	0	$T=0$ state
	$|1,1,0>$	ϵ_2	
	$|1,0,1>$	ϵ_3	
	$|0,2,0>$	$2\epsilon_2$	
	$|0,1,1>$	$\epsilon_2 + \epsilon_3$	
	$|0,0,2>$	$2\epsilon_3$	

c) Let $\beta \equiv 1/kT$.

$$Z_F(T) = e^{-\epsilon_2 \beta} + e^{-\epsilon_3 \beta} + e^{-(\epsilon_2+\epsilon_3)\beta}$$

$$Z_B(T) = 1 + e^{-\epsilon_2 \beta} + e^{-\epsilon_3 \beta} + e^{-2\epsilon_2 \beta} + e^{-(\epsilon_2+\epsilon_3)\beta} + e^{-2\epsilon_3 \beta}$$

d)

$$Z_F(T) \approx e^{-\epsilon_2 \beta} + e^{-\epsilon_3 \beta}$$

$$
\begin{aligned}
<E>_F &= -\frac{1}{Z_F}\frac{\partial Z_F}{\partial \beta} \\[2mm]
&\approx \frac{\epsilon_2 e^{-\epsilon_2 \beta} + \epsilon_3 e^{-\epsilon_3 \beta}}{e^{-\epsilon_2 \beta} + e^{-\epsilon_3 \beta}} = \frac{\epsilon_2 + \epsilon_3 e^{-(\epsilon_3-\epsilon_2)\beta}}{1 + e^{-(\epsilon_3-\epsilon_2)\beta}} \\[2mm]
&= \frac{\left[\epsilon_2 + \epsilon_3 e^{-(\epsilon_3-\epsilon_2)\beta}\right]\left[1 - e^{-(\epsilon_3-\epsilon_2)\beta}\right]}{1 - \left(e^{-(\epsilon_3-\epsilon_2)\beta}\right)^2} \\[2mm]
&= \frac{\epsilon_2 + (\epsilon_2 - \epsilon_3)e^{-(\epsilon_3-\epsilon_2)\beta} - \epsilon_3 e^{-2(\epsilon_3-\epsilon_2)\beta}}{1 - e^{-2(\epsilon_3-\epsilon_2)\beta}} \\[2mm]
&\approx \underline{\epsilon_2 + (\epsilon_3 - \epsilon_2)e^{-(\epsilon_3-\epsilon_2)\beta}}
\end{aligned}
$$

This result shows a finite $< E >$ at $T = 0$ and energy gap behavior with $\Delta = \epsilon_3 - \epsilon_2$.

$$< E >_B = -\frac{1}{Z_B}\frac{\partial Z_B}{\partial \beta}$$

$$\approx \frac{\epsilon_2 e^{-\epsilon_2\beta}}{1 + e^{-\epsilon_2\beta}}$$

$$\approx \underline{\epsilon_2 e^{-\epsilon_2\beta}}$$

This result shows $< E >= 0$ at $T = 0$ and energy gap behavior with $\Delta = \epsilon_2$.

Problem 2: A Number of Two-State Particles

The two single-particle states available are indicated below.

$$\psi_1 \qquad \rule{3cm}{0.4pt} \qquad \epsilon = \Delta$$

$$\psi_0 \qquad \rule{3cm}{0.4pt} \qquad \epsilon = 0$$

a) Use the number of particles in the upper single particle state as the index for the many-particle states:

$$|n_0, n_1 >= |N - n_1, n_1 > \qquad \text{and} \qquad \underline{E_{n_1} = n_1\Delta}$$

$$n_1 = 0, 1, 2, \cdots N \qquad \Rightarrow \underline{N + 1} \text{ many-particle states}$$

b) Let $\beta \equiv 1/kT$.

$$Z(N,T) = \sum_{n_1=0}^{N} e^{-n_1\Delta\beta} = \sum_{n_1=0}^{N}\left(e^{-\Delta\beta}\right)^{n_1}$$

$$= \sum_{n_1=0}^{\infty}\left(e^{-\Delta\beta}\right)^{n_1} - \sum_{n_1=N+1}^{\infty}\left(e^{-\Delta\beta}\right)^{n_1}$$

$$= \sum_{n_1=0}^{\infty}\left(e^{-\Delta\beta}\right)^{n_1} - \left(e^{-\Delta\beta}\right)^{N+1}\sum_{m=0}^{\infty}\left(e^{-\Delta\beta}\right)^{m}$$

$$= \frac{1}{1 - e^{-\Delta\beta}} - \frac{e^{-(N+1)\Delta\beta}}{1 - e^{-\Delta\beta}}$$

$$= \underline{\frac{1 - e^{-(N+1)\Delta\beta}}{1 - e^{-\Delta\beta}}}$$

c)

$$p(n_1) = \frac{1}{Z}e^{-n_1\Delta/kT} = \underline{\frac{1 - e^{-\Delta/kT}}{1 - e^{-(N+1)\Delta/kT}}\, e^{-n_1\Delta/kT}}$$

d) If the particles are distinguishable, similar, and non-interacting, then

$$Z_d(N,T) = (Z_{\text{one particle}})^N = \left(1 + e^{-\Delta/kT}\right)^N$$

Problem 3: Identical Particle Effects in Rotational Raman Scattering

a) Since the Cl nuclei have half-integer spin, $I = 3/2$, they are Fermions and their wave-function must be anti-symmetric under interchange of the two particles. The two-particle wavefunction consists of two factors, one representing the spatial motion (rotation) of the particles and one representing their spins. The spatial wavefunctions are eigenfunctions of the angular momentum with quantum numbers L and m_L. The wavefunctions with even L are symmetric; those with odd L are anti-symmetric. Thus the states of even L must be paired with spin states that are anti-symmetric and those with odd L must be paired with symmetric spin states. The nuclear spin states are formed by adding two angular momenta, each of magnitude 3/2. The resulting total spin can have the values $I_T = 3, 2, 1$ and 0. The state with the highest magnitude of the total spin is always symmetric, and the symmetry alternates as the total magnitude is stepped down, by 1 each time. So there are a total of 10 symmetric spin states $((2\cdot 3 + 1) + (2\cdot 1 + 1))$, and 6 anti-symmetric spin states $((2\cdot 2 + 1) + (2\cdot 0 + 1))$.

The rotational energy levels increase monotonically with L, so the spin states, and the associated degeneracy, must alternate between the symmetric and anti-symmetric values. For the spin degeneracies that would be 6, 10, 6, 10, $\cdots$. Thus the ratio of the two separate intensity envelopes is $\underline{6/10 = 3/5 = 0.60}$.

b) Treating L as a continuous variable gives the expression for the envelope of the series of delta functions in the Raman spectrum. We find the spot where that envelope is a maximum.

$$\frac{d}{dL}(2L+1)\exp[-L(L+1)\Theta_R/T] = (2 - (\Theta_R/T)(2L+1)^2)\exp[-L(L+1)\Theta_R/T]$$

$$= 0$$

$$(2L+1)^2 = 2(T/\Theta_R)$$

$$L \approx \underline{\sqrt{\frac{T}{2\Theta_R}}}$$

c) For N_2

$$L \approx \sqrt{\frac{300}{2 \times 2.9}} \approx 7$$

The N_2 spectrum in the notes peaks near the 8th line, which arrises from transitions from the $L = 7$ level.

For N_2

$$L \approx \sqrt{\frac{300}{2 \times 0.35}} \approx 21$$

so one expects the rotational Raman spectrum to peak near the 22nd line.

d) Since the two nuclei are two different isotopes they are not identical particles. All 16 nuclear spin states are allowed with each of the rotational states. The spectrum will evolve smoothly with L. The intensities of the lines will not alternate.

Problem 4: Langmuir Isotherm

a) The number of ways one can place N identical atoms on $M \geq N$ distinct sites, given that each site can hold no more than one atom is equal to the number of ways of choosing N objects from M when order does not count:

$$\underline{\frac{M!}{(M - N)!N!}}$$

b)

$$Z = \sum_{\text{states}} \exp[-E_{\text{state}}/k_B T] = \sum_n g_n \exp[-E_n/k_B T] = \underline{\frac{M!}{(M - N)!N!} \exp[N\epsilon_0/k_B T]}$$

c)

$$F = -k_B T \ln Z$$

$$\ln Z = N\epsilon_0/k_B T + M \ln M - M - (M - N)\ln(M - N) + (M - N) - N \ln N + N$$

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

$$= -k_B T[\epsilon_0/k_B T + 1 + \ln(M - N) - 1 - 1 - \ln N + 1]$$

$$= \underline{-\epsilon_0 - k_B T \ln\left(\frac{M - N}{N}\right)}$$

d) From the lecture we have the chemical potential of a classical non-interacting gas in 3 dimensions.

$$\mu_{\text{bulk}} = k_B T \ln n \lambda^3(T)$$

In equilibrium the two chemical potentials must be equal.

$$\mu_{\text{surface}} = \mu_{\text{bulk}}$$

$$-\epsilon_0 - k_B T \ln \left(\frac{1-f}{f} \right) = k_B T \ln n \lambda^3(T)$$

$$\ln \left(\frac{f}{1-f} \right) = \epsilon_0/k_B T + \ln n \lambda^3(T)$$

$$\left(\frac{1-f}{f} \right) = \lambda^3(T) \, e^{\epsilon_0/k_B T} \, n$$

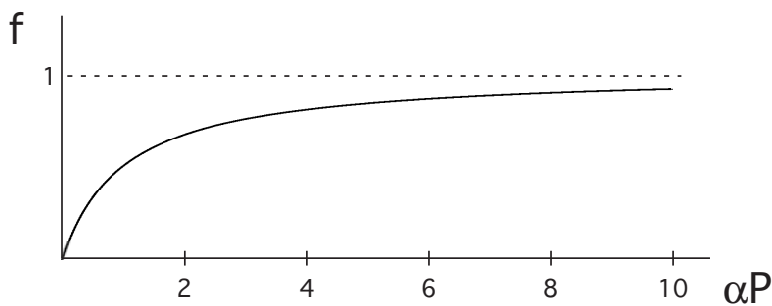$$f = \frac{\lambda^3(T) \, e^{\epsilon_0/k_B T} \, n}{1 + \lambda^3(T) \, e^{\epsilon_0/k_B T} \, n}$$

$\lambda(T) \equiv h/\sqrt{2\pi m k_B T}$ so if $h = 0$ then $f = 0$.

e) Use the ideal gas law $P = (N/V)k_B T = nk_B T$ to change the variable representing the bulk gas from number density n to pressure P.

$$f = \frac{\alpha P}{1 + \alpha P}$$

where the parameter α depends on temperature through the expression

$$\alpha = \left(\lambda^3(T)/k_B T \right) \, e^{\epsilon_0/k_B T} = h^3 (2\pi m)^{-3/2} (k_B T)^{-5/2} \, e^{\epsilon_0/k_B T}$$

Problem 5: Information Theory Approach to Statistical Mechanics

a)

$$p_{\text{state}} = \frac{1}{\Omega} \quad \text{and} \quad \Omega = \sum_{\text{states}} (1)$$

$$
\begin{aligned}
S_I &= -k_B \sum_{\text{states}} \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right) \\
&= k_B \left(\frac{1}{\Omega}\right) \ln(\Omega \sum_{\text{states}} (1) \\
S_I &= \underline{k_B \ln \Omega = S_{\text{microcanonical}}}
\end{aligned}
$$

b)

$$p_{\text{state}} = \frac{e^{-\beta E_{\text{state}}}}{Z}, \quad Z = \sum_{\text{states}} e^{-\beta E_{\text{state}}} \quad \text{and} \quad F(T,V) = -k_B T \ln Z$$

$$
\begin{aligned}
S_I &= -k_B \sum_{\text{states}} p_{\text{state}} \ln\left(\frac{e^{-\beta E_{\text{state}}}}{Z}\right) \\
&= -k_B \sum_{\text{states}} p_{\text{state}} (-\beta E_{\text{state}} - \ln Z) \\
&= \frac{1}{T} <E> + k_B \ln Z \underbrace{\sum_{\text{states}} p_{\text{state}}}_{1} \\
&= \frac{1}{T}(U + k_B T \ln Z) \\
S_I &= \underline{\frac{1}{T}(U - F) = \frac{1}{T}(U - (U - TS)) = S_{\text{canonical}}}
\end{aligned}
$$

c)

$$\frac{\partial}{\partial p_{N,\nu}}\left[S_I + \lambda_1(1) + \lambda_U U + \lambda_{\bar{N}}\bar{N}\right] = \frac{\partial}{\partial p_{N,\nu}}\sum_{N,\nu}\left[-k_B\, p_{N,\nu}\ln p_{N,\nu} + \lambda_1 p_{N,\nu} + \lambda_U E_{N,\nu}p_{N,\nu} + \lambda_{\bar{N}}Np_{N,\nu}\right]$$

$$= -k_B\left(\frac{p_{N,\nu}}{p_{N,\nu}} + \ln p_{N,\nu}\right) + \lambda_1 + \lambda_U E_{N,\nu} + \lambda_{\bar{N}}N] = 0$$

$$\ln p_{N,\nu} = \lambda_1/k_B - 1 + (\lambda_U/k_B)\,E_{N,\nu} + (\lambda_{\bar{N}}/k_{\bar{B}})\,N$$

d)

$$k_B\sum_{N,\nu}\left[p_{N,\nu}\ln p_{N,\nu}\right] = \sum_{N,\nu}\left[(\lambda_1 - k_B)p_{N,\nu} + \lambda_U E_{N,\nu}p_{N,\nu} + \lambda_{\bar{N}}\,Np_{N,\nu}\right]$$

$$-S_I = (\lambda_1 - k_B) + \lambda_U U + \lambda_{\bar{N}}\,\bar{N}$$

We can solve the given expression for the grand potential for S and find

$$-S = \frac{\Phi}{T} - \frac{U}{T} + \frac{\mu}{T}\,\bar{N}$$

If the information theory entropy is to equal the thermodynamic entropy then we must make the following assignments.

$$(\lambda_1 - k_B) = \frac{\Phi}{T}$$

$$\lambda_U = -\frac{1}{T}$$

$$\lambda_{\bar{N}} = \frac{\mu}{T}$$

Substituting these back into the expression we found for the probabilities we found in c) gives

$$\ln p_{N,\nu} = \frac{\Phi}{k_B T} - \frac{E_{N,\nu}}{k_B T} + \frac{\mu N}{k_B T}$$

$$p_{N,\nu} = \exp[(\mu N - E_{N,\nu})/k_B T]\exp[\Phi/k_B T]$$

Recall that the grand partition function $\mathcal{Z}$ is related to the grand potential Φ by the relation

$$\Phi(T, V, \mu) = -k_B T \ln \mathcal{Z}$$

Using this brings us to the final form for the probability density in the grand canonical ensemble.

$$p_{N,\nu} = \exp[(N\mu - E_{N,\nu})/k_B T] / \mathcal{Z}$$

Problem 6: Maxwell Relations

Begin with the internal energy U.

$$dU = TdS - PdV + \mu dN$$

Holding V constant and recognizing that the cross derivatives of T and μ must be equal since U is a state function gives

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

Inverting the partial derivatives on both sides gives us

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

Now examine the Helmholtz free energy $F \equiv U - TS$.

$$dF = -SdT - PdV + \mu dN$$

Hold the temperature constant and equate the cross derivatives of μ and P.

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

Continuing alphabetically, let's examine the Gibbs free energy $G \equiv U - TS + PV$.

$$dG = -SdT + VdP + \mu dN$$

Hold P fixed and equate the cross derivatives of μ and T

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

Finally examine the enthalpy $H \equiv U + PV$.

$$dH = TdS + VdP + \mu dN$$

Hold S constant and equate the cross derivatives of mu and V.

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

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