

# Problem Review Session 5

## PHYS 741

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*Disclaimer:* The problems below are not my own making but are taken from Pathria's Statistical Mechanics (PSM) and past qualifying exams from UNC (Qual).

### Practice Problems

1. (**Qual 2015 SM-1**) Consider an ideal gas in a one-dimensional channel of length  $L$ . The energy of the particle is given by  $E = (p^2/2m) - \varepsilon_0$ .

(a) Show, using the classical approach, that the partition function of one particle is given by

$$Q_1(T, L) = \frac{L}{\lambda} e^{\varepsilon_0/kT} \quad \text{and} \quad \lambda = \frac{h}{\sqrt{2\pi mkT}}$$

(b) Calculate the chemical potential of this system of  $N$  indistinguishable particles at temperature  $T$ .

Reminder:  $\int_0^\infty e^{-x^2} dx = \sqrt{\pi}/2$ .

2. (**Qual 2012 SM-5**) A cylinder of radius  $R$  and length  $L$  contains  $N$  molecules of mass  $m$  of an ideal gas at temperature  $T$ . The cylinder rotates about its axis with an angular velocity  $\omega$ . Find a change in the free energy of the gas  $\Delta A$ , as compared to that at rest.
3. (**PSM 3.31**) Study the statistical mechanics of a system (i.e. calculate the entropy, chemical potential, pressure, internal energy and heat capacities) of  $N$  "Fermi oscillators," which are characterized by only 2 eigenvalues, namely 0 and  $\varepsilon$ . (This is similar to Problem 6.3 in Huang only you are now doing it from canonical approach.)

### Additional Problem

4. (**PSM 3.18**) Show that for a system in the canonical ensemble

$$\langle (\Delta E)^3 \rangle = k^2 \left[ T^4 \left( \frac{\partial C_V}{\partial T} \right)_V + 2T^3 C_V \right].$$

Verify that for an ideal gas

$$\left\langle \left( \frac{\Delta E}{U} \right)^2 \right\rangle = \frac{2}{3N} \quad \text{and} \quad \left\langle \left( \frac{\Delta E}{U} \right)^3 \right\rangle = \frac{8}{9N^2}.$$

5. (**PSM 3.26**) The energy eigenvalues of an  $s$ -dimensional harmonic oscillator can be written as  $\varepsilon_j = (j + s/2)\hbar\omega$ .

Show that the  $j$ th energy level has a multiplicity of  $(j+s-1)!/j!(s-1)!$ . Evaluate the partition function, and the major thermodynamic properties of a system of  $N$  such oscillators, and compare your results with a corresponding system of  $sN$  one-dimensional oscillators. Show in particular that the chemical potential  $\mu_s = s\mu_1$ .

# Session 5 Problem 1

Qual 2015 SM-1

a) In general, the partition for a single particle in 1-D is given by

$$Q_1 = \frac{1}{h} \int dp dq e^{-\beta H}$$

where  $H$  is the Hamiltonian of the system

For this problem  $H = p^2/2m - \epsilon_0$

$$\Rightarrow Q_1 = \frac{1}{h} \int_0^L dq \int_0^\infty dp e^{-\beta(\frac{p^2}{2m} - \epsilon_0)}$$

$$= \frac{L}{h} e^{\beta \epsilon_0} \int_0^\infty dp e^{-\beta p^2/2m}$$

$$= \frac{L}{h} e^{\beta \epsilon_0} \frac{\Gamma(1/2)}{\sqrt{\beta/2m}} = \sqrt{\frac{2m\pi kT}{h^2}} L e^{\epsilon_0/kT}$$

$$\Rightarrow Q_1 = \frac{L}{\lambda} e^{\epsilon_0/kT}$$

w/  $\lambda = \sqrt{\frac{2m\pi kT}{h^2}}$  as defined in the problem

b) The chemical potential is given by the Maxwell relation

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

The Helmholtz free energy is related to the partition function by

$$A = -kT \ln Q_N$$

when  $Q_N$  is the partition function for all  $N$  particles

For indistinguishable, independent particles

$$Q_N = \frac{1}{N!} Q_1^N = \frac{1}{N!} \left( \frac{L}{\lambda} \right)^N e^{\epsilon_0 N/kT}$$

$$\Rightarrow \frac{A}{kT} = N \ln N - N - N \ln(L/\lambda) - N \epsilon_0/kT$$

← where we use Stirling's approx:  $\ln N! \approx N \ln N - N$

$$\Rightarrow \mu = \left( \frac{\partial A}{\partial N} \right)_{T,L} = kT \ln \left( \frac{N\lambda}{L} \right) - \epsilon_0 = \mu$$

# Session 5 Problem 2

Qual 2012 SM-5

There has been a lot of debate about what exactly the Hamiltonian is for the system. Would a gas even notice that the cylinder is spinning at first since the only way a gas molecule "knows the cylinder" is if it comes in contact w/ the cylinder wall since it's a non-interacting ideal gas.

So we will assume the gas has had sufficient time to know that the cylinder is spinning. To be honest, I still haven't convinced which Hamiltonian is correct, but it should have the form

$$H = \frac{p^2}{2m} \pm \frac{1}{2} m \omega^2 r^2$$

+ refers to centripetal potential

- refers to centrifugal potential

↳ basically is there a real central potential or is there just some inertial force?

I'll assume (-) for this problem, but the calculations are virtually the same if you use a positive potential. I use the negative sign because it makes intuitive sense that the gas minimizes its energy by clustering along the outer edges of the container as compared to the center of the cylinder.

The change in free energy is given by

$$\Delta A = -kT (\ln Q_N^{\text{rot}} - \ln Q_N^{\text{non-rot}}) = -kT \ln \frac{Q_N^{\text{rot}}}{Q_N^{\text{non-rot}}}$$

$Q_N^{\text{rot}}$  = rotational partition function ;  $Q_N^{\text{non-rot}}$  = non-rotating partition function

We can calculate the partition functions from the single particle partition function

$$Q_1^{\text{rot}}(\omega) = \int \frac{d^3p d^3q}{h^3} e^{-\beta(\frac{p^2}{2m} - \frac{1}{2} m \omega^2 r^2)} ; Q_1^{\text{non-rot}} = Q_1^{\text{rot}}(\omega=0)$$

With  $Q_N = (Q_1)^N / N!$

These functions only differ by their integrations over  $r$ , therefore all other integrals cancel.

$$\begin{aligned} \Rightarrow \Delta A &= -NkT \ln \frac{Q_1^{\text{rot}}}{Q_1^{\text{non-rot}}} = -NkT \ln \left[ \frac{\int_0^R e^{\beta m \omega^2 r^2 / 2} r dr}{\int_0^R r dr} \right] \\ &= -NkT \ln \left[ \frac{2 \int_0^{\beta m \omega^2 R^2 / 2} e^x dx}{\beta m \omega^2 R^2} \right] \quad \leftarrow x \equiv \frac{\beta m \omega^2 r^2}{2} ; dx = \beta m \omega^2 r dr \end{aligned}$$

$$\Rightarrow \Delta A = -NkT \ln \left[ \frac{1}{\lambda} (e^\lambda - 1) \right] \quad \lambda \equiv \frac{\beta m \omega^2 R^2}{2}$$

# Session 5 Problem 3

Pathna 3.31

First we calculate the partition function for a single particle, which is given by

$$Q_1 = \sum_{i=1}^2 e^{-\beta \epsilon_i} = 1 + e^{-\beta \epsilon} \quad \beta = 1/kT$$

Since we are dealing with  $N$  identical, distinguishable particles, the full partition function is given by

$$Q_N = [Q_1]^N = (1 + e^{-\beta \epsilon})^N$$

We relate the partition function of statistical mechanics to thermodynamics through the Helmholtz potential

$$A = -kT \ln Q_N = -NkT \ln(1 + e^{-\beta \epsilon})$$

For this problem we want to calculate  $S$ ,  $\mu$ ,  $P$ ,  $U$ ,  $C_V$ , &  $C_p$  which are related by Maxwell relations

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} ; \mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} ; P = -\left(\frac{\partial A}{\partial V}\right)_{V,T} ; U = A + TS$$

$$\Rightarrow S = Nk \ln(1 + e^{-\beta \epsilon}) + \frac{N\epsilon e^{-\beta \epsilon}}{T(1 + e^{-\beta \epsilon})} = Nk \left[ \ln(1 + e^{-\beta \epsilon}) + \frac{\beta \epsilon}{e^{\beta \epsilon} + 1} \right] = S$$

$$\Rightarrow \mu = -kT \ln(1 + e^{-\beta \epsilon})$$

$$\Rightarrow P = 0 \quad \therefore C_p = C_V$$

$$\Rightarrow U = \frac{N\epsilon}{e^{\beta \epsilon} + 1} \quad \frac{-N\epsilon^2 e^{\beta \epsilon}}{(1 + e^{\beta \epsilon})^2} \frac{\partial \beta}{\partial T}$$

Using  $U$  we can calculate  $C_p$  &  $C_V$  from

$$C_p = C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{Nk(\beta \epsilon)^2 e^{\beta \epsilon}}{(1 + e^{\beta \epsilon})^2}$$