

## Phys 430 - 3<sup>rd</sup> HOMEWORK

1. Describe the following concepts using your own words. (Do not write equations or copy the explanation in some book):

- (a) Le Chaterlier's Principle

*Solution:*

If a system is disturbed by some change in the external condition, the system will behave in such a way as to reduce the effect. For example, if the system is heated, there will be processes in the system that will reduce the temperature.

- (b) Nernst's theorem

*Solution:*

Is the theorem that states that the entropy of any system is zero at absolute zero,  $T = 0K$ . In classical thermodynamics, entropy is defined up to an additive constant. This theorem states that the entropy of any system at absolute zero is a universal constant which can be set to be zero.

- (c) Microcanonical Distribution

*Solution:*

If one considers the evolution of a closed system, the average of any macroscopic property of the system can be defined as a time average over a sufficiently long time. It is also possible to take many copies of the same system at different times and consider the average over all these copies at a single instant. This set of the system is called the Microcanonical ensemble, and their distribution in phase space is called the microcanonical distribution. The energy, linear momentum and angular momentum of all the copies in the ensemble is the same and hence the distribution is zero at any point in phase space that does not have these fixed values of energy and momentum. In microcanonical ensemble, it is also assumed that the distribution has the same constant value at the points where it is not zero, hence the probability of the system to be in any state consistent with the initial energy, linear momentum and angular momentum is constant.

- (d) Positiveness of  $C_P$  and negativeness of  $\left(\frac{\partial P}{\partial V}\right)_X$ ,  $X = S, T$

*Solution:*

The entropy of a system at in equilibrium is a maximum, not just a minimum. Hences, besides requiring the first derivatives of the entropy to be zero in equilibrium, it is also necessary that the second derivatives satisfy certain inequalities, so that it will be a maximum. These inequalities imply that  $\left(\frac{\partial P}{\partial V}\right)_X > 0$ ,  $X = S, T$  and that  $C_V > 0$ . Since  $C_P > C_V$ , it is also true that  $C_P > 0$

2. Consider the question in the second homework which we could not solve using microcanonical ensemble: Consider an ideal gas enclosed in a volume  $V$  and consisting of  $N$  point particles whose energy momentum relation is given by  $\varepsilon = cp$  whare  $c$  is some constant and  $p$  is the magnitude of the momentum of the particles. For this gas, calculate:

- (a) Calculate the velocity distribution for a single particle.

*Solution:*

The momentum probability distribution is:

$$dw(\vec{p}) = Ae^{-\beta K(p)} d^3p \quad (1)$$

where  $A$  is fixed by the normalization condition, i.e.  $1 = \int dw(p)$  and  $K(p) = E(p) = cp$  since there is no potential energy. Since we will be interested not in the direction but on the mangitude of the momentum, we can integrate over the direction to obtain the magnitud distribution. Using  $d^3p = p^2 dp d\Omega$  where  $d\Omega = \sin \theta d\theta d\phi$  is the solid angle and integrating over the angles, we obtain:

$$dw(p) = A4\pi e^{-\beta cp} p^2 dp \quad (2)$$

substituting  $p = mv$ , one obtains the velocity distribution:

$$dw(v) = Am^3 4\pi e^{-\beta cmv} v^2 dv \quad (3)$$

The normalization condition gives the value  $A = \frac{c^3}{8\pi T^3}$  for the constant  $A$  and hence the velocity distribution for a single particle is:

$$dw(v) = \frac{c^3 m^3}{2T^3} e^{-\beta mcv} v^2 dv \quad (4)$$

- (b) Calculate the average energy for a single particle

*Solution:*

The average energy for a single particle is given by

$$\begin{aligned}\langle E \rangle &= \int E dw(\vec{p}) = mc \int_0^\infty v dw(v) = mc \frac{c^3 m^3}{2T^3} \int_0^\infty dv v^3 e^{-\beta mc v} \\ &= mc \frac{c^3 m^3}{2T^3} \frac{6T^4}{m^4 c^4} = 3T\end{aligned}\quad (5)$$

- (c) Calculate  $C_V$  for  $N$  particles

*Solution:*

For  $N$  particles, the energy of the system is, using the result of the previous part,  $E = N(3T) = 3NT$ . Then

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3N \quad (6)$$

- (d) Calculate the thermodynamic potentials  $F$ ,  $E$ ,  $W$ ,  $\Phi$  and  $\Omega$  for the system

*Solution:*

In the class we had shown that the free energy  $F$  for a system of  $N$  non interacting particles can be written as:

$$F = -NT \ln \frac{eZ_1}{N} \quad (7)$$

where  $Z_1$  is the partition function of a single particle:

$$\begin{aligned}Z_1 &= \sum_{allstates} e^{-\beta E_n} \\ &= \int \frac{d^3 p d^3 q}{(2\pi\hbar)^3} e^{-\beta cp} \\ &= \frac{V}{(2\pi\hbar)^3} \int p^2 dp d\Omega e^{-\beta cp} \\ &= \frac{V}{8\pi^3 \hbar^3} 4\pi \frac{T^3}{c^3} \\ &= \frac{VT^3}{2\pi^2 c^3 \hbar^3}\end{aligned}\quad (8)$$

And hence the free energy  $F$  is given by:

$$F = -NT \ln \frac{eT^3 V}{2\pi^2 c^3 \hbar^3 N} \quad (9)$$

The the entropy is the negative of the derivative of  $F$  with respect to  $T$  and constant  $N$  and  $V$ :

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} = N \ln \frac{eT^3V}{2\pi^2c^3\hbar^3N} + 3N = -\frac{F}{T} + 3N \quad (10)$$

and hence the energy is:

$$E = F + TS = 3NT \quad (11)$$

consistant with the result of the previous section.

The pressure is the negative derivative of the free energy  $F$  with respect to  $V$  at constant  $T$  and  $N$ :

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T,N} = \frac{NT}{V} \quad (12)$$

and hence the heat function is:

$$W = E + PV = 3NT + NT = 4NT \quad (13)$$

The free energy  $\Phi$  is defined as  $\Phi = F + PV$  and hence

$$\begin{aligned} \Phi &= -NT \ln \frac{eT^3V}{2\pi^2c^3\hbar^3N} + NT \\ &= -NT \ln \frac{T^3V}{2\pi^3c^3\hbar^3N} \end{aligned} \quad (14)$$

The theromodynamical potential  $\Omega$  is defined as  $\Omega = F - \mu N$  and hence we need the chemical potential  $\mu$ . The chemical potential is defined as the derivative of  $F$  with respect to  $N$  at constant  $T$  and  $V$ :

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} = -T \ln \frac{eT^3V}{2\pi^2c^3\hbar^3N} + T = -\frac{F}{N} + T \quad (15)$$

Hence

$$\Omega = F - \mu N = -NT = -PV \quad (16)$$

- (e) What is the chemical potential for this system?

*Solution:*

The chemical potential is calculated in the previous section as:

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} = -T \ln \frac{eT^3V}{2\pi^2c^3\hbar^3N} + T = -T \ln \frac{T^3V}{2\pi^2c^3\hbar^3N} \quad (17)$$

3. Consider two objects with heat capacities  $C_1$  and  $C_2$  at temperatures  $T_1$  and  $T_2 < T_1$  respectively.

- (a) If the two object are brought into direct contact, heat will flow from the hotter to the colder object until equilibrium is established. (This will not be a reversible process) What will be the temperature in equilibrium?

*Solution:*

Let  $T$  be the final temperature of the system. When the system reaches equilibrium, both systems will have the same temperature  $T$ . The heat released by the hot object during this time would be:  $Q_{released} = C_1(T_1 - T)$  and the heat absorbed by the cold object will be  $Q_{absorbed} = C_2(T - T_2)$ . The absorbed heat by the cold object has to be equal to the heat release by the hot object and hence  $C_2(T - T_2) = C_1(T_1 - T)$ . Solving for  $T$ , one obtains for the equilibrium temperature:

$$T = \frac{C_1T_1 + C_2T_2}{C_1 + C_2} \quad (18)$$

- (b) If the two systems are brought to equilibrium using a reversible process. What is the maximum work that can be extracted from the system?

*Solution:*

Let the equilibrium temperature be  $T_{eq}$ . Then the total heat released by the hotter system will be  $Q_{released} = C_1(T_1 - T)$ , the heat absorbed by the colder system will be  $Q_{absorbed} = C_2(T - T_2)$  and the work done will be  $W_{max} = Q_{released} - Q_{absorbed} = (C_1T_1 + C_2T_2) - (C_1 + C_2)T_{eq}$ .

To achieve equilibrium through a reversible process, one can use infinitesimal Carnot cycles that take  $dQ_1$  amount of heat from the hot object, do  $dW = dQ_1\eta$  amount of work and dump  $dQ_2$

amount of heat to the colder reservoir. For the process to be an equilibrium process, we need to have

$$dS_1 + dS_2 = -\frac{dQ_1}{T_1} + \frac{dQ_1}{T_2} = 0 \quad (19)$$

Note that the temperatures  $T_1$  and  $T_2$  appearing here are the instantaneous temperatures when the heat is taken by the Carnot cycle and the minus sign in front of  $dQ_1$  is due to the fact the  $dQ_1$  is the heat released by the system.

Using  $dQ_1 = -C_1 dT_1$  (again the minus sign is due to the fact the  $dQ_1$  is the heat released) and  $dQ_2 = C_2 dT_2$  one obtains:

$$-C_1 \frac{dT_1}{T_1} = C_2 \frac{dT_2}{T_2} \quad (20)$$

Integrating both sides from their initial values to the their final values:

$$-C_1 \int_{T_1}^{T_{eq}} \frac{dT_1}{T_1} = C_2 \int_{T_2}^{T_{eq}} \frac{dT_2}{T_2} \quad (21)$$

Integrating the integrals and solving for  $T_{eq}$ , one obtains for the equilibrium temperature:

$$T_{eq} = T_1^{\frac{C_1}{C_1+C_2}} T_2^{\frac{C_2}{C_1+C_2}} \quad (22)$$

and hence the maximum work becomes:

$$W_{max} = (C_1 T_1 + C_2 T_2) - (C_1 + C_2) T_1^{\frac{C_1}{C_1+C_2}} T_2^{\frac{C_2}{C_1+C_2}} \quad (23)$$

(c) In the last case, what will be the equilibrium temperature?

*Solution:*

The equilibrium temperature is already evaluated in the last part:

$$T_{eq} = T_1^{\frac{C_1}{C_1+C_2}} T_2^{\frac{C_2}{C_1+C_2}} \quad (24)$$

4. Consider a gas enclosed in a cylinder of radius  $R$ . What would be the density profile of this gas if the cylinder is rotated at a constant angular frequency  $\Omega$  around its axis of symmetry? (Hint: in the reference frame

in which the cylinder is at rest, the effects of rotation can be mimicked by an external potential of the form:  $U(r) = -\frac{1}{2}m\Omega^2 r^2$  where  $r$  is the distance from the central axis)

*Solution:*

The density profile does not change if one changes the frame of reference. And hence consider the non-inertial reference frame rotating with the cylinder. In this reference frame, the cylinder is at rest but there is a pseudo potential energy. The position distribution of the particles is given by:

$$dw(\vec{q}) = Ae^{-\beta U(q)} d^3q = Ae^{\frac{m\Omega^2}{2T} r^2} \quad (25)$$

The constant  $A$  is fixed by the normalization, but for this problem, the exact value is not relevant for us.

The density of particles at a given point is proportional to the probability that you will find a particle at that point. Hence, the density at the point  $\vec{q}$  would be given by:

$$\rho(\vec{q}) = \rho_0 e^{\frac{m\Omega^2}{2T} r^2} \quad (26)$$

where  $\rho_0$  is the density of the particles along the axis of the cylinder and  $r = |\vec{q}|$ .