PHYS 430 - First Midterm SOLUTIONS

1. Comment on the following concepts (Just writing equations will not gain you any points): (3 points each, 21 points total)

   (a) Negative Temperatures
   Solution:
   Temperature is a measure of how entropy increases as the energy of the system increases. Hence negative temperature just means that the entropy of the system decreases as the energy of the system it increasing. This is possible only if the energy of the system is bounded from above. Negative temperature systems are hotter than positive temperature systems in the sense that if you bring into contact a system with negative temperature and another system with pisitive temperature, heat flows from negative temperatures to positive temperatures.

   (b) Micro canonical Distribution
   Solution:
   In micro canonical distribution it is assumed that the probability of the system to be in a state which satisfies the constraints imposed on the system such as the total energy, linear and angular momentum, is constant. That is if you consider two states that have the same energy and momentum, the probability that the system will be in any one of these states is the same. This is called micro canonical distribution.

   (c) P-V Diagram
   Solution:
   P-V space is the plane which has P as one of the axis and V as the other axis. If a system is in mechanical equilibrium, it has a definite pressure and volume at each instant. Hence any process which results in the change of P and/or V or the system will correspond to a trajectory in the P-V diagram.

   (d) Thermodynamical Potential
   Solution:
   Thermodynamical potentials such as the free energies, the heat function, energy, entropy, etc, are functions that contain all the information about the system. By differentiating the thermodynamical potentials it is possible to obtain the macroscopic properties of a given system and also starting from any one of the

thermodynamical potentials, it is possible to obtain all the others.

(e) Reversible process
Solution:
A reversible process is a process in which the entropy of the whole system remains constant. By applying the operations in reverse order, one can trace back the process and come back to the initial state.

(f) Ergodic Hypothesis
Solution:
Ergodic hypothesis is the assumption that the system will come close to any point in phase space that is consistant with the constraints imposed on the system infinitely many times. And the density of the trajectory will be uniform.

(g) Entropy
Solution:
Mathematically, entropy is the logarith of the number of states that the system can be found it. It measures the disorder of a system and the lack of our knowledge about the state of the system. If one considers a closed system, the entropy of the closed system will always increase or at most remain constant.

2. Consider a gas of identical particles confined to move only on the surface of a rectangular area of side length L. The energy momentum relation for the particles is given as $\epsilon = \alpha(p_x^2 + p_y^2)$ where p_x and p_y are the components of the momenta along two perpendicular directions on the surface and α is some constant. Calculate the entropy of this system if the system has energy E. (10 points). Calculate the temperature, T(5 points), of the system and the surface tension σ(5 points) of the system. (Hint: For a two dimensional system, $dE = TdS - \sigma dA$ where dA is a differential change of the area of the system and σ is called the surface tension) (20 points)
Solution:
Just like the 3D case, we will first calculate $\Gamma(E)$, the number of states that have the energy less then or equal to E. The energy of a state is

given by the $2N$ positive integers n_x^i, n_y^i as:

$$E = \alpha \frac{\hbar^2}{L^2} \sum_{i=1}^{N} (n_x^{i2} + n_y^{i2}) \qquad (1)$$

Using the same reasoning as in the $3D$ case, $\Gamma(E)$ is proportional to the volume of the $2N$ dimensional sphere with radius $R = \sqrt{\frac{EA}{\alpha\hbar^2}}$ where $A = L^2$:

$$
\begin{aligned}
\Gamma(E) &= \frac{1}{N!} \frac{1}{2^{2N}} \text{volume of sphere} \\
&= \frac{1}{N! 2^{2N}} \int d^{2N}x\, \theta(R - r) \\
&= \frac{1}{N! 2^{2N}} \int_0^R dr\, r^{2N-1} \int d\Omega_{2N} \\
&= \frac{1}{N! 2^{2N}} \frac{2\pi^N}{(N-1)!} \frac{R^{2N}}{2N} \\
&= \frac{1}{N!^2} \left(\frac{E\pi A}{4\alpha\hbar^2} \right)^N \qquad (2)
\end{aligned}
$$

where in the first line, the factor $1/N!$ is to take into account the fact the that particles are identical, and the factor $1/2^{2N}$ is included to consider the volume of only part of the sphere where all the coordinates are positive (since $n_x^i, n_y^i > 0$)

Once $\Gamma(E)$ is known, $\Delta\Gamma(E)$ can easily be obtained:

$$
\begin{aligned}
\Delta\Gamma(E) &= \frac{\partial \Gamma(E)}{\partial E} \Delta E \\
&= \frac{1}{N!(N-1)!} \left(\frac{E\pi A}{4\alpha\hbar^2} \right)^N \frac{\Delta E}{E} \qquad (3)
\end{aligned}
$$

The entropy is obtained by taking the logarithm os $\Delta\Gamma(E)$:

$$
\begin{aligned}
S &= \log \Delta\Gamma(E) \\
&= N \log \frac{E\pi A}{4\alpha\hbar^2} - 2\log N! + \log \frac{\Delta E}{E} \\
&= N \log \left(\frac{\pi}{4\alpha\hbar^2} \left(\frac{E}{N}\right) \left(\frac{A}{N}\right) e^2 \right) \qquad (4)
\end{aligned}
$$

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where in order to obtain the last equality, Stirling's approximation is used and terms negligible compared to N are neglected.

In order to obtain the temperature, we need to differentiate S w.r.t. E:

$$T^{-1} = \frac{\partial S}{\partial E} = \frac{\partial}{\partial E}\left(N \log E + \cdots\right) = \frac{N}{E} \tag{5}$$

where $\cdots$ are terms in entropy that do not depend on E and hence go to zero after differentiation. Hence:

$$T = \frac{E}{N} \tag{6}$$

Since $dE = TdS - \sigma dA$, $dS = \frac{1}{T}dE + \frac{\sigma}{T}dA$. Hence

$$\sigma = T\left(\frac{\partial S}{\partial A}\right)_E \tag{7}$$

Using the result for the entropy, we have:

$$\sigma = T\frac{\partial}{\partial A}\left(N \log A + \cdots\right) = \frac{NT}{A} \tag{8}$$

where in this expressions, $\cdots$ stand for terms that do not depend on A.

3. Consider a Carnot' cycle that uses the Van Der Waals gas as the working gas. Show explicitly that the efficiency of this Carnot' cycle is given by $\eta = 1 - \frac{T_{cold}}{T_{hot}}$. In order to show this you need to go through several steps: (61 points)

   (a) First you need to calculate the adiabatic curve for the Van der Waals gas. To calculate the adiabatic curve, consider the derivative

   $$\left(\frac{\partial V}{\partial T}\right)_S$$

   First change your variables to (V, T) from (S, T) and obtain the relation between the volume and temperature in an adiabatic process. Then substituting T from the Van der Waals equation of state, show that in an adiabatic process:

   $$(V - Na)^{5/3}\left(P + a\frac{N^2}{V^2}\right) = const$$

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(15 points)
Solution:

$$
\begin{aligned}
\left(\frac{\partial V}{\partial T}\right)_S &= \frac{\partial(V,S)}{\partial(T,S)} = \frac{\partial(V,S)/\partial(V,T)}{\partial(T,S)/\partial(V,T)} \\
&= \frac{(\partial S/\partial T)_V}{-(\partial S/\partial V)_T}
\end{aligned}
\tag{9}
$$

Using the Maxwell relation,

$$
\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V
\tag{10}
$$

and the definition of C_V:

$$
C_V = T\left(\frac{\partial S}{\partial T}\right)_V
\tag{11}
$$

one obtains:

$$
\left(\frac{\partial V}{\partial T}\right)_S = -\frac{1}{T}\frac{C_V}{(\partial P/\partial T)_V}
\tag{12}
$$

Differentiation the given equation of state with respect to T at constant volume, one obtains:

$$
\left(\frac{\partial P}{\partial T}\right)_V (V - Nb) = N
\tag{13}
$$

or

$$
\left(\frac{\partial P}{\partial T}\right)_V = \frac{N}{V - Nb}
\tag{14}
$$

Moreover, from the expression for the energy of the Van der Walls gas,

$$
C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}N
\tag{15}
$$

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and hence

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{1}{T}\frac{3}{2}N\frac{(V-Nb)}{N} = -\frac{3(V-Nb)}{2T} \tag{16}$$

In terms of the differentials in an adiabatic process, we have

$$\frac{dV}{V-Nb} = -\frac{3}{2}\frac{dT}{T}$$

$$d\ln(V-Nb) + \frac{3}{2}d\ln T = 0$$

$$d\ln\left[(V-Nb)T^{\frac{3}{2}}\right] = 0 \tag{17}$$

Hence, in an adiabative process, for the Van der Waals Gas,

$$(V-Nb)T^{\frac{3}{2}} = const \tag{18}$$

Expression T in terms of P and V using the equation of state:

$$(V-Nb)^{\frac{5}{2}}\left(P + a\frac{N^2}{V^2}\right)^{\frac{3}{2}} = const \tag{19}$$

or taking the $2/3^{rd}$ power, we obtain:

$$(V-Nb)^{\frac{5}{3}}\left(P + a\frac{N^2}{V^2}\right) = const \tag{20}$$

which concludes our derivation of the adiabatic equation for the Van der Waals' gas.

(b) Draw the P-V diagram for the Carnot cycle. (5 points)
Solution:
The P-V diagram for the Carnot cycle using the Van der Waals' gas is qualitatively similar to the carnot cycle that uses the ideal gas.

(c) Calculate the work done on the gas, the heat absorbed by the gas, and the change in the internal energy of the gas for each of the 4 stages of the Carnot cycle. (You need to calculate $3 \times 4 = 12$ results. 3 points each of the results (36 points)
Solution:

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i. The $1 \rightarrow 2$ process:
   This part of the cycle is an isothermal process and hence we can use the equation of state to calculate the work done during this process:

$$
\begin{aligned}
W_{12} = \int_{V_1}^{V_2} -PdV &= -\int_{V_1}^{V_2} \left(\frac{NT_1}{V - Nb} - a\frac{N^2}{V^2} \right) dV \\
&= -\left(NT_1 \ln(V - Nb) + a\frac{N^2}{V} \right) \bigg|_{V=V_1}^{V=V_2} \\
&= -NT_1 \ln \frac{V_2 - Nb}{V_1 - Nb} - aN^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right)
\end{aligned}
\tag{21}
$$

Since the internal energy of the Van der Waals gas depend also on its volume, during the process, the internal energy of the Van der Waals' gas changes by:

$$
\Delta E = -aN^2 \Delta \frac{1}{V} = -aN^2 \left(\frac{1}{V_2} - \frac{1}{V_1} \right)
\tag{22}
$$

The amount of heat absorbed by the system during this process is then

$$
Q_{12} = \Delta E - W_{12} = NT_1 \ln \frac{V_2 - Nb}{V_1 - Nb} > 0
\tag{23}
$$

Hence during this process, the system absorbes heat.

ii. The $2 \rightarrow 3$ process
   This part of the cycle is adiabative, and hence there is no heat exchange: $Q_{23} = 0$. The work done during this process is:

$$
\begin{aligned}
W_{23} = \Delta E &= \Delta \left(\frac{3N}{2}T - a\frac{N^2}{V} \right) \\
&= \frac{3N}{2}(T_2 - T_1) - aN^2 \left(\frac{1}{V_3} - \frac{1}{V_2} \right)
\end{aligned}
\tag{24}
$$

iii. The $3 \rightarrow 4$ process:
   The calculation of this process is the same as the $1 \rightarrow 2$ process, with the replacements: $V_1 \rightarrow V_3$, $V_2 \rightarrow V_4$, $T_1 \rightarrow T_2$

since the starting point in this process is the point 3 and the
final point is the point 4. Hence:

$$W_{34} = -NT_2 \ln \frac{V_4 - Nb}{V_3 - Nb} - aN^2 \left(\frac{1}{V_4} - \frac{1}{V_3} \right)$$

$$\Delta E = -aN^2 \Delta \frac{1}{V} = -aN^2 \left(\frac{1}{V_4} - \frac{1}{V_3} \right)$$

$$Q_{34} = \Delta E - W_{34} = NT_2 \ln \frac{V_4 - Nb}{V_3 - Nb} < 0 \qquad (25)$$

Hence, during this stage, the system releases heat to the cold
reservoir.

iv. The $4 \rightarrow 1$ process:
The calculations of this process is the same as the $2 \rightarrow 3$
process with the replacement: $V_2 \rightarrow V_4$, $V_3 \rightarrow V_1$, $T_1 \rightarrow T_2$, $T_2 \rightarrow T_1$. Hence:

$$Q_{41} = 0$$

$$W_{41} = \Delta E = \frac{3N}{2}(T_1 - T_2) - aN^2 \left(\frac{1}{V_1} - \frac{1}{V_4} \right) \quad (26)$$

(d) Calculate the efficiency (5 points)
Solution:
In order to calculate the efficiency, we need the total heat absorbed
and the net work done by the system. The net work done can be
obtained either by summing the works done in each stage of the
process, i.e. $W = W_{12} + W_{23} + W_{34} + W_{41}$, or from the conservation
of energy $W = Q_{absorbed} - Q_{released}$. where $Q_{absorbed} = Q_{12} = NT_1 \ln \frac{V_2 - Nb}{V_1 - Nb}$ and $Q_{released} = -Q_{34} = NT_2 \ln \frac{V_3 - Nb}{V_4 - Nb}$ where the $-$
sign is due to the fact the Q_{34} is negative. Then the efficiency is:

$$\eta = \frac{W}{Q_{absorbed}} = 1 - \frac{Q_{released}}{Q_{absorbed}}$$

$$= 1 - \frac{T_2 \ln \frac{V_3 - Nb}{V_4 - Nb}}{T_1 \ln \frac{V_2 - Nb}{V_1 - Nb}} \qquad (27)$$

To simplify the ration of the logarithms, note that the points 2
and 3 lie on the same adiabatic curve and hence

$$(V_2 - Nb)T_1^{\frac{3}{2}} = (V_3 - Nb)T_2^{\frac{3}{2}} \qquad (28)$$

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and similarly the points 1 and 2 lie on the same adiabatic curve and hence

$$(V_1 - Nb)T_1^{\frac{3}{2}} = (V_4 - Nb)T_2^{\frac{3}{2}} \tag{29}$$

Deviding both equations side by side, one obtains:

$$\frac{V_2 - Nb}{V_1 - Nb} = \frac{V_3 - Nb}{V_4 - Nb} \tag{30}$$

that is the arguments of the logarithms appearing in the efficiency are the same, and hence they cancel. Thus

$$\eta = 1 - \frac{T_2}{T_1} \tag{31}$$

as it should be.

(Hint: The Van der Walls equation of state is

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NT$$

and the energy of a Van der Waals gas can be written as:

$$E = \frac{3}{2}NT - a\frac{N^2}{V}$$

)

4. Calculate the rate of change of the temperature of a Van der Waals' gas undergoing a Joule Thompson process. (Hint: a Joule Thompson process is a process that changes the pressure of the gas keeping the heat function constant). The relevant information about the Van der Waals gas is given in the previous problem.
Solution:
The rate of change of the temperature is given by the derivative:

$$\left(\frac{\partial T}{\partial P}\right)_W \tag{32}$$

Using the Jacobian matrices, this can be written as:

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{\partial(T,W)}{\partial(P,W)} = \frac{\partial(T,W)/\partial(T,V)}{\partial(P,W)/\partial(T,V)} \tag{33}$$

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Let's study the numerator and the denominator seperately: The numerator can be written explicetly as:

$$\frac{\partial(T,W)}{\partial(T,V)} = \left(\frac{\partial W}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T \tag{34}$$

where we have used $dW = TdS + VdP$. Using the Maxwell relations, this can be rewritten as:

$$\frac{\partial(T,W)}{\partial(T,V)} = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T \tag{35}$$

In the third problem we had already obtained in Eq. (14) that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{N}{V - Nb} \tag{36}$$

In order to evaluate the derivative $\left(\frac{\partial P}{\partial V}\right)_T$, we need to differentiate equation of state w.r.t volume at treating temperature as a constant to obtain

$$\left[\left(\frac{\partial P}{\partial V}\right)_T - 2a\frac{N^2}{V^3}\right](V - Nb) + \left(P + a\frac{N^2}{V^2}\right) = 0 \tag{37}$$

or

$$\begin{aligned}\left(\frac{\partial P}{\partial V}\right)_T &= -\frac{P + a\frac{N^2}{V^2}}{V - Nb} + 2a\frac{N^2}{V^3} \\ &= -\frac{NT}{(V - Nb)^2} + 2a\frac{N^2}{V^3}\end{aligned} \tag{38}$$

Substituting in Eq. (35), we obtain:

$$\frac{\partial(T,W)}{\partial(T,V)} = -\frac{N^2bT}{(V - Nb)^2} + 2a\frac{N^2}{V^2} \tag{39}$$

The denominator of Eq. (32) can be written as:

$$\frac{\partial(P,W)}{\partial(T,V)} = \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial W}{\partial V}\right)_T - \left(\frac{\partial W}{\partial T}\right)_V\left(\frac{\partial P}{\partial V}\right)_T \tag{40}$$

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Substituting

$$\left(\frac{\partial W}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial V}\right)_T \tag{41}$$

and

$$\left(\frac{\partial W}{\partial T}\right)_V = C_V + V\left(\frac{\partial P}{\partial T}\right)_V \tag{42}$$

Eq. (40) reduces to

$$\frac{\partial(P,W)}{\partial(T,V)} = T\left(\frac{\partial P}{\partial T}\right)_V^2 - C_V\left(\frac{\partial P}{\partial V}\right)_T \tag{43}$$

Substituting Eqs. (15), (14)and (38) into Eq. (43) we obtain:

$$\frac{\partial(P,W)}{\partial(T,V)} = \frac{5}{2}\frac{N^2 T}{(V-Nb)^2} - 3a\frac{N^3}{V^3} \tag{44}$$

Hence the rate of change of the temperature of a Van der Waals' gas in a JT process is:

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{-\frac{N^2 bT}{(V-Nb)^2} + 2a\frac{N^2}{V^2}}{\frac{5}{2}\frac{N^2 T}{(V-Nb)^2} - 3a\frac{N^3}{V^3}}$$

$$\simeq -\frac{2b}{5} + \frac{4a}{5T} + \mathcal{O}(\frac{N}{V}) \tag{45}$$

Note that, when $a = 0 = b$, i.e. the gas is an ideal gas, the temperature does not change, a result that we had obtained in the class for the ideal gas.