6CCP3212 Statistical Mechanics Review Problems for Thermal physics

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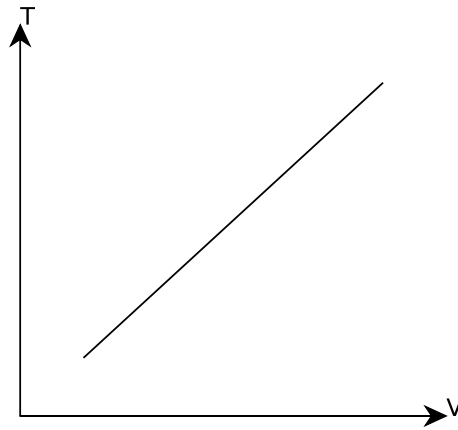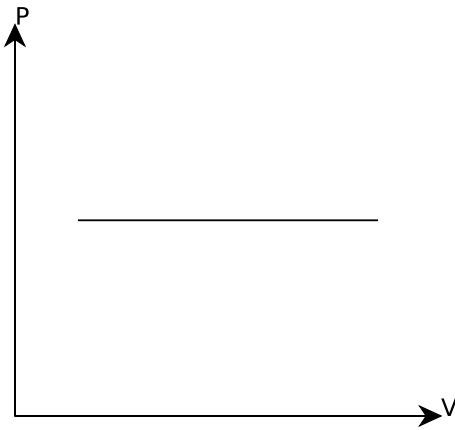
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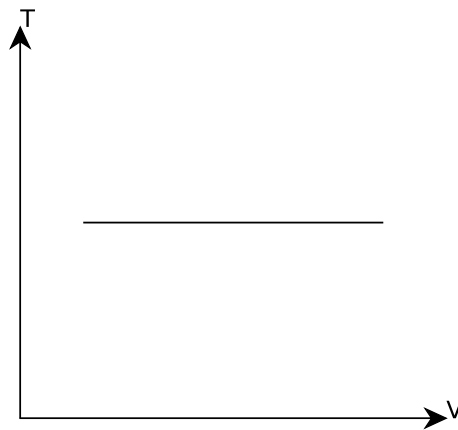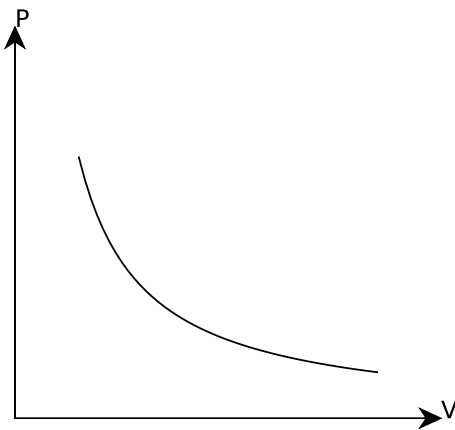
1) Consider the equation of state for an ideal gas

$$PV = Nk_bT \tag{1}$$

where N is the number of particles and k_b is the Boltzmann constant. Draw the following curves on a (i) $P - V$ phase diagram and a (ii) $T - V$ phase diagram.
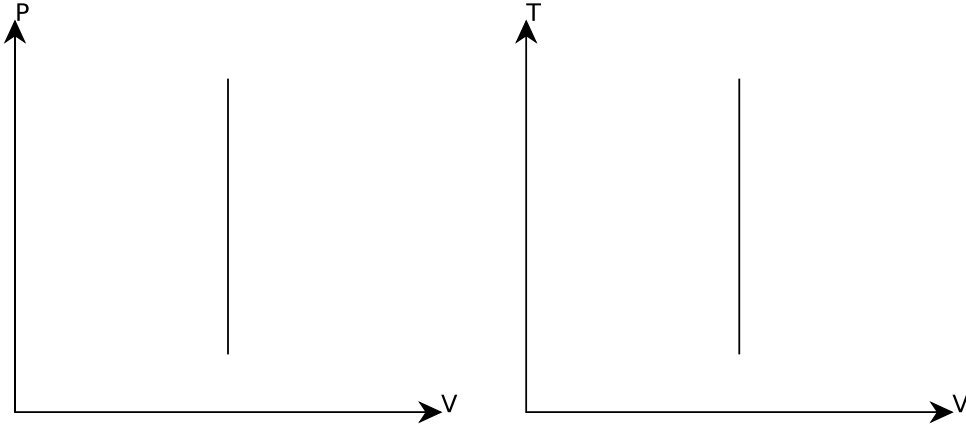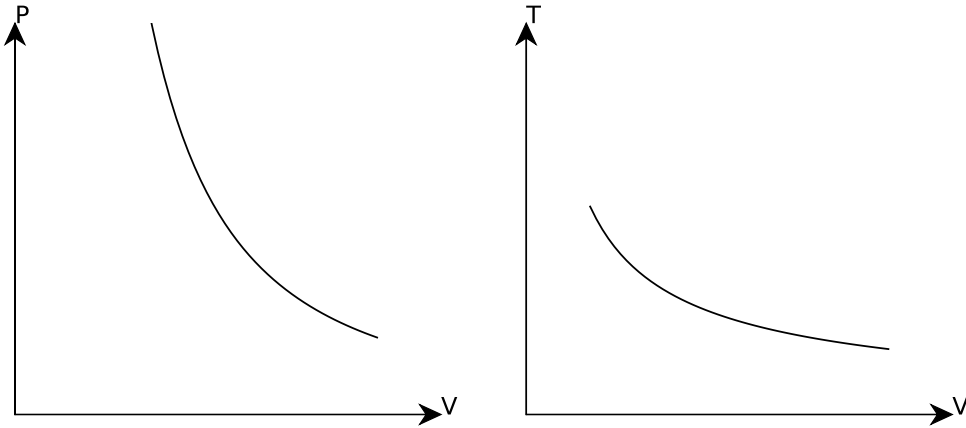
- An isobaric (constant pressure) curve.

- An isothermal (constant temperature) curve.

- A isochoric (constant volume) curve.

- An isentropic (constant entropy) curve.

2) Find the partial derivatives $\partial f/\partial x$ and $\partial f/\partial y$ for the following functions:

- $f(x,y) = \sqrt{x^2 + y^2}$
  Use chain rule: $\dfrac{\partial f}{\partial x} = \dfrac{x}{\sqrt{x^2 + y^2}}$ $\dfrac{\partial f}{\partial y} = \dfrac{y}{\sqrt{x^2 + y^2}}$

- $f(x,y) = \frac{1}{x+y^2}$
  Use chain rule: $\dfrac{\partial f}{\partial x} = -\dfrac{1}{(x+y^2)^2}$ $\dfrac{\partial f}{\partial y} = -\dfrac{2y}{(x+y^2)^2}$

- $f(x,y) = \frac{\log(x+y)}{x^2}$
  Use quotient rule: $\dfrac{\partial f}{\partial x} = \dfrac{1}{x^4(x+y)}$ $\dfrac{\partial f}{\partial y} = \dfrac{1}{x^2(x+y)}$

3) Find the total derivative df/dt for the following functions

- $f(x, y) = x^y$, $x(t) = t^2$, $y(t) = t$.

  To find the total derivative we repeatedly apply the chain rule.

  $$\frac{df}{dt} = \frac{\partial f}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial f}{\partial y}\frac{\partial y}{\partial t}$$
  $$= 2yx^{y-1}t + x^y \log x$$
  $$= 2t^{2t} + t^{2t} \log t^2$$

  We could also subtitute in the expressions to get $f(t)$ and then differentiate but this approach usually requires less algebra.

- $f(x) = \log x^2$, $x(y, z) = y^2 + z$, $y(t) = t^{-1}$, $z(t) = t$.

  Using the same idea:

  $$\frac{df}{dt} = \frac{\partial f}{\partial x}\left[\frac{\partial x}{\partial y}\frac{\partial y}{\partial t} + \frac{\partial x}{\partial z}\frac{\partial z}{\partial t}\right]$$
  $$= \frac{2}{x}\left[-2yt^{-2} + 1\right]$$
  $$= \frac{-4t^{-3} + 2}{t^{-2} + t}$$

- $f(x, y, t) = xyt$, $x(t) = t^2$, $y(x, t) = x + t$.

  Lets do this one by sustituing in the expressions for x and y.

  $$f(t) = t^2(t^2 + t)t$$
  $$= t^5 + t^4$$
  $$\frac{df}{dt} = 5t^4 + 4t^3$$

3) For the following differentials, state whether they are *exact* or *inexact*.

- $dz = xdx + ydy$.

  A differential $dz = P(x, y)dx + Q(x, y)dy$ is exact if it there is a function $z(x, y)$ such that $P(x, y) = \frac{\partial z}{\partial x}$ and $Q(x, y) = \frac{\partial z}{\partial y}$. This can only be the case if and only if $\frac{\partial P}{\partial y} = \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial z \partial y} = \frac{\partial Q}{\partial x}$ for any well behaved function. We can use the first and last terms of the previous equations to check if a differential is exact.

  $$dz = P(x, y)dx + Q(x, y)dy = xdx + ydy$$

  So we must have: $\frac{\partial P}{\partial y} = \frac{\partial Q}{\partial x}$ which is satisfied as both are zero.

- $dz = ydx - xdy$.

  For this we have $\frac{\partial P}{\partial y} = 1$ and $\frac{\partial Q}{\partial x} = -1$, so dz is an inexact differential.

Integrate the above equations $\int dz$ from $(x, y) = (0, 0)$ to $(x, y) = (1, 1)$, using

- The path $x = y$.

- The path $(x, y) = (0, 0)$ to $(x, y) = (0, 1)$ and then $(x, y) = (0, 1)$ to $(x, y) = (1, 1)$.

  We will start with $dz = xdx + ydy$ along the path $x = y$ which we can parameterise by $t = x = y$.

  $$\int xdx + ydy = 2\int_0^1 tdt = 1$$

For $(x, y) = (0, 0)$ to $(x, y) = (0, 1)$ we have:

$$\int xdx + ydy = \int_0^1 tdt = \frac{1}{2}$$

For $(x, y) = (0, 1)$ to $(x, y) = (1, 1)$ we have:

$$\int xdx + ydy = \int_0^1 tdt = \frac{1}{2}$$

so for the full path $(x, y) = (0, 0)$ to $(x, y) = (0, 1)$ and then $(x, y) = (0, 1)$ to $(x, y) = (1, 1)$ we get 1, the same as the path $x = y$ which is to be expected as we know that line integrals of exact differentials are path independent.

Now we integrate $dz = ydx - xdy$ along the path $x = y$.

$$\int ydx - xdy = \int_0^1 tdt - \int_0^1 tdt = 0$$

For $(x, y) = (0, 0)$ to $(x, y) = (0, 1)$ we have:

$$\int ydx - xdy = \int_0^1 tdt = \frac{1}{2}$$

For $(x, y) = (0, 1)$ to $(x, y) = (1, 1)$ we have:

$$\int ydx - xdy = \int_0^1 dt = 1$$

and we see that the integral of an in exact differential is path dependent.

4) What is a **closed** system? What is an **open** system? Which of the following systems are open, and which are closed.
A closed system cannot exchange matter with it's surroundings but it can exchange energy via heat and work. An open system can exchange both matter and energy with it's surrounding.

- An refrigerator kept at $T = 273K$: closed.

- A car engine: open, requires fuel and produces exhaust

- A blender: closed.

- A hydroelectric dam: open, requires a constant stream of running water.

- A thermal flask with lid on: closed.

5) Work done *on* a thermodynamic system is given by $PdV = -dW$ (the bar in d for $đ$ is explained in the first chapter of the lecture notes, but for now you don't have to worry about it). Find the work done on the an ideal gas system $PV = Nk_bT$ to change it from (P_1, V_1) to (P_2, V_2).
To calculate the work done on the system we will integrate W $= \int_{V_1}^{V_2} -PdV$ along a reversible path, i.e. the system must be at equilibrium along all points in the path.

- An isobaric process $P = C$ where C is a constant.
  An isobaric process occurs at a constant pressure. Since P is constant the integral is trival and we get $W = -P(V_2 - V_1)$.

- An isochoric process $V = C$ where C is a constant.

  An isochoric proccess occurs at a constant volume: $dV = 0 \implies dW = -PdV = 0$. Thus, the total work done is zero.

- A **polytropic process** is given by the following curve

$$PV^n = C \tag{2}$$

  where C is a constant and $n > 1$ is the polytropic constant. Show that the work done on the system to change it from (P_1, V_1) to (P_2, V_2) is given by

$$W = \frac{P_1V_1 - P_2V_2}{1 - n} \ . \tag{3}$$

  What happens when $n = 1$? Argue that your results suggest that work is path-dependent (we will prove this in Homework 1).

  We begin by using the equation of state to express the pressure as a function of volume in the integral and doing the integration to find the work done.

$$W = -\int_{V_1}^{V_2} PdV$$
$$= -C\int_{V_1}^{V_2} V^{-n}dV$$
$$= -\frac{C}{1-n}\left[V^{1-n}\right]_{V_1}^{V_2}$$
$$= -\frac{1}{1-n}\left[V_2P_2 - V_1P_1\right]$$
$$= \frac{P_1V_1 - P_2V_2}{1-n} \ .$$

  When $n = 1$ the integration above is no longer valid. The equation of state will become equivalent to the ideal gas law at a constant temperature. We will tackle that case in the next part of this question. Since we can vary the path taken between the initial and final conditions (described by the equation of state) by changing n and we know that the work done also depends on n, we can thus deduce that the work done is path dependent.

- An isothermal process $T = C$ where C is a constant.

  For an isothermal expansion we have $PV = Nk_bT = Nk_bC$ for some constant C. We can calculate the work writing P in terms of V and integrating along the path parameterised by V.

$$W = -\int_{V_1}^{V_2} PdV$$
$$= -Nk_bC\int_{V_1}^{V_2} \frac{1}{V}dV$$
$$= -Nk_bC\log\frac{V_2}{V_1}$$

6) Consider a mole of ideal gas at $T = 400K$ with equation of state $PV = Nk_bT$ expanding reversibly and isothermally from $V = 10L$ to $V = 30L$, where L is a unit of volume. Calculate the increase in entropy S of this process.

The key to this question is realising that the change in internal energy ΔU for this process is zero sine it's an ideal gas. Since an ideal gas consists only interacting when they collide, the internal energy only depends on the temperature, which is constant, therefore the internal energy also remains constant. The

first law states $\Delta U = Q + W = T\Delta S + W = 0$. So we can use this to calculate the change in entropy S if we know W and T. We can use our result from the last question to calculate W.

$$S = -\frac{W}{T}$$

$$= Nk_b \log \frac{V_2}{V_1}$$

$$= R \log 3$$

$$= 8.31\text{JK}^{-1} \times 1.01 = 9.13\text{JK}^{-1}$$

7) A heat engine absorbs heat Q_1 reversibly from a reservoir at $T = 300K$ and expel heat Q_2 reversibly to a reservoir at $T = 200K$. This engine has an efficiency of 25% while doing $W = 125J$ of work in a cycle of work.

- Calculate Q_1.
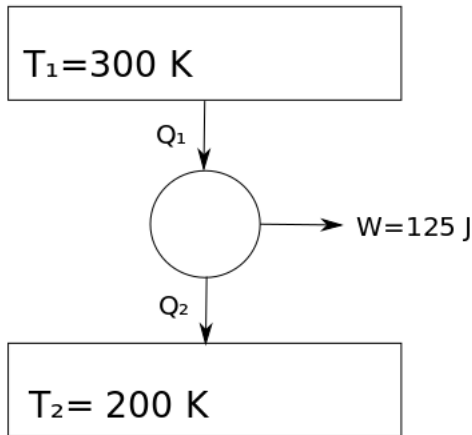
The efficiency $\eta = 0.25$ is defined as the ratio of the energy you get out and the energy you put in.

$$\eta = \frac{W}{Q_1} \implies Q_1 = 4W = 500\text{J}$$

- Calculate the change in entropy of the engine system for this single cycle of work.

For one complete cycle the change in internal energy is zero, so by the first law we must have:

$Q_1 - Q_2 = W \implies Q_2 = 375\text{J}$

To calculate the change in entropy we must be careful about signs. The entropy change for a heat transfer is given by $\Delta S = \frac{Q}{T}$.

So for the the whole cycle we have:

$$\Delta S_{\text{engine}} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

$$= \frac{500}{300}\text{JK}^{-1} - \frac{375}{200}\text{JK}^{-1} = -0.208\text{JK}^{-1}$$

- Calculate the change in the entropy for the two reservoirs, and show that the *total* change of entropy for the entire reservoir-engine systems is zero for a reversible process.

This can be calculated similarly, using the same sign convention for the the heats (+ve corresponding heat is going into the system).

$$\Delta S_{\text{reservoir 1}} = -\frac{Q_1}{T_1} = -\frac{500}{300} \text{JK}^{-1} = -1.67 \text{JK}^{-1}$$

$$\Delta S_{\text{reservoir 2}} = +\frac{Q_2}{T_2} = \frac{375}{200} \text{JK}^{-1} = 1.88 \text{JK}^{-1}$$

Summing the entropy changes for the engine and both reservoirs, we get:

$$\Delta S_{\text{total}} = \Delta S_{\text{engine}} + \Delta S_{\text{reservoir 1}} + \Delta S_{\text{reservoir 2}} = 0$$

which is what is expected for a reversible cycle due to Clausius' theorem.

8) A mole of a monoatomic ideal gas are at a temperature of $T = 300$ K. The gas expands reversibly and isothermally to twice its original volume. Calculate the work done by the gas, the heat supplied, and the change in internal energy.

This question is similar to 6. The change in internal energy is zero and we can use our derived expression for the work done on an ideal gas in an isothermal expansion and obtain the heat supplied using the first law.

$$W = -RT \log \frac{V_2}{V_1}$$

$$= -8.31 \text{JK}^{-1} \times 300 \text{K} \times \log 2$$

$$= -1730 \text{J}$$

From the first law we know $Q = -W$, so the heat supplied is $Q = 1730 \text{J}$