

## PROBLEM SET 2

- 1) **(15 pts)** The critical point is the unique point on the original van der Waals isotherms where both the first and second derivatives of  $P$  with respect to  $V$  (at fixed  $T$ ) are zero. Use this fact to show that

$$V_c = 3Nb, \quad P_c = \frac{1}{27} \frac{a}{b^2}, \quad \text{and} \quad kT_c = \frac{8}{27} \frac{a}{b}$$

*Hint:* Use Text Eq. 5.49 (p. 180) discussed in lecture (you'll need to take 1st, 2nd partial derivatives, set them to 0, solve and substitute)

- 2) **(15 pts)** In the van der Waals equation of state, define dimensionless volumes, pressures, and temperatures by the equations  $v = V/V_c$ ,  $p = P/P_c$ , and  $t = T/T_c$ , where  $V_c$ ,  $P_c$  and  $T_c$  are the critical volume, pressure, and temperature associated with the van der Waals equation of state (discussed in lecture). Show that in terms of these dimensionless quantities, the van der Waals equation of state is given by

$$\left(p + \frac{3}{v^2}\right)(v - 1/3) = \frac{8}{3}t$$

- 3) **(10 pts)** An ideal *monatomic* gas has initial pressure  $P_0$  and occupies initial volume  $V_0$ . The gas undergoes an *adiabatic* expansion in which the volume is doubled. Calculate in terms of  $P_0$  and  $V_0$
- a) the final pressure of the gas
  - b) work done by the gas during the expansion
  - c) the change in its enthalpy during the expansion

4) **(10 pts)** Text, Problem 1.36

- 5) **(20 pts)** The equation of state of a particular (non-ideal!) gas is given by  $(P + b)V = nRT$ , where  $b$  is a constant. The internal energy of the gas is given by  $U = U_0 + naT + bV$ , where  $a$  and  $U_0$  are two more constants.

a) Derive an expression for the differential work done on the gas when its volume is increased from  $V$  to  $V + dV$  at temperature  $T$ . Your result should depend on  $T$ ,  $V$ ,  $dV$ , and the constants  $R$  and  $b$ .

b) Determine the corresponding differential increase in  $U$  (note that  $dT$  is not zero!) and then use the first law of thermodynamics to find the differential heat transfer into the gas.

c) Using the result of part b, show that the constant volume heat capacity for this gas is given by  $C_V = na$ .

d) Show that for a constant pressure process for this gas,  $dV = [nR/(P + b)]dT$ , and then following a similar procedure as in parts a), b), and c), determine the constant pressure heat capacity for the gas. Finally, show that  $C_p - C_V = nR$ , as for an ideal gas.

- 6) **(15 pts)** The pressure associated with the electromagnetic radiation within a closed container of volume  $V$  and temperature  $T$  depends only on the temperature and is given by  $P = aT^4/3$ , where  $a$  is a constant. The internal energy associated with the radiation is given by  $U = aT^4V$ .

a) With the help of the first law of thermodynamics, show that if the volume of the container is doubled in an isothermal process, then the heat transfer into the container is given by  $Q = (4/3)aT^4V$ .

b) In an adiabatic process,  $dQ=0$  so that  $PdV = -dU$ . Use this relation to derive a differential relation connecting  $V$  and  $T$  in an adiabatic process;

then integrate this relation to show that in an adiabatic process,  $VT^3$  is constant for this system.

7) **(10 pts) Text, Problem 1.49** – you should assume here that the result of the combustion, liquid water, has negligible volume. Also, note that the work done on the gas is positive (its volume is reduced), so that the work done on the atmosphere is negative.

8) **(5 pts) Text, Problem 1.53**

9) **Optional Extra Credit: 15 pts undergraduates, 10 pts graduates** (points obtained can be added towards 1st exam if you end up with  $< 100\%$  on the exam) – due date: on exam date (Sep 28, 2023)

Use your preferred programming language (ideally, Python or C++ ROOT) to plot the reduced van der Waals equation of state (problem 2),  $p(v, t)$  versus  $v$  for isotherms,  $t = 0.8, 0.9, 1.0, 1.10$ . Set the y-axis range  $p : [-1, 2.5]$ , x-axis range  $v : [-0.1, 4]$  for plot ranges

*hint1:* re-arrange the van der Waals equation to obtain  $p(v, t)$ , then for each of the isotherms, you should have 4 different equation (curves) only in terms of  $v$ , e.g.,  $p(v, t = 0.8)$ ,  $p(v, t = 0.9)$ ,  $p(v, t = 1.0)$ ,  $p(v, t = 1.1)$

*hint2:* How smooth the function  $p(v)$  comes out depends on the number of points (or states) you assign to your independent variable,  $v$ . For example, you should set a range of  $v = [v_{min}, 1.2, 100]$ , where  $v_{min} > 1/3$  (I would suggest,  $(v_{min} = 1/3 + 1e-6)$ ). Note that this range is different than the plot range mentioned above. The  $v_{min}$  here a physical requirement imposed by the finite volume of the gas molecules, otherwise, you will end up with negative volumes.

*hint3:* when plotting, don't use markers (data points), rather use lines to connect the points, but don't display the points themselves, so it appears like a continuous curve. The result should look like multiple curves, which you should assign a different color for each isotherm to distinguish them, and properly display a legend with the different isotherms, associated with each curve.

To receive full credit, you **MUST** print out the plot with the different overlayed curves as well as the code/script you wrote to produce the plots.

This extra credit problem is a good opportunity to learn about or exercise your programming language skills, which are an essential part of doing scientific research. **If you don't understand, ASK ! There are NO SILLY questions.**  
**You are encouraged to ask questions regarding this extra credit exercise.**