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Advanced Statistical Physics, SS 2017
Sheet 6

Problem 1: **(2 points)**

Suppose that you want to fill your friend's room (area = 10 m^2, height = 2.5 m) with balloons. You will fill the balloons with gas in your room, and then sneak them into your friend's room. To facilitate the transportation of the balloons, you will cool them with liquid nitrogen (77.4° K), and then carry them in an ice chest (volume = 1 m^3).

a) If the balloons are filled with an ideal gas, how many trips do you need to make in order to fill the room?

b) If the balloons are filled with air, will you need to make more or fewer trips?

Problem 2: **(5 points)**

In 1873, van der Waals proposed an equation of state that predicted more precisely the observed behavior of gases:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}, \tag{1}$$

where a and b are constants that depend on the type of the gas. The molar internal energy and volume are u and v respectively. Equation (1) is also interesting from a theoretical point, because it exhibits a phase transition and a critical point. The following plot shows some isotherms of a van der Waals gas in the (p, v) plane:

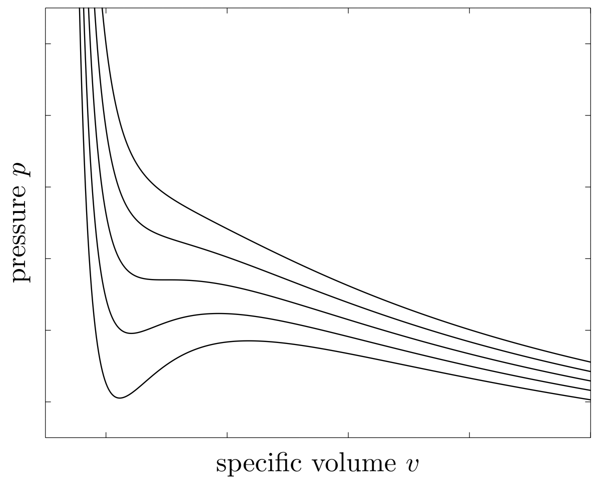

Figure 1: Isotherms of the van der Waals gases for five different temperatures. The center isotherm is the critical one. The constants are $a = 0.01$ and $b = 1$.

a) The isotherms in the figure are not labelled. Show from (1) that the temperature is lowest for the lowest isotherm, and highest for the uppermost one.

b) Explain why the regions where $\left(\frac{\partial p}{\partial v}\right)_T < 0$ are thermodynamically unstable.

c) The center isotherm is the one belonging to the critical temperature. The critical temperature T_* is the smallest temperature for which there are no points where $\left(\frac{\partial p}{\partial v}\right)_T < 0$. The critical point is the inflexion point on the critical isotherm. Find the temperature T_*, the pressure p_* and the volume v_* at the critical point.

d) Show that the van der Waals equation of state can be written as

$$\bar{p} = \frac{8\bar{T}}{3\bar{v} - 1} - \frac{3}{\bar{v}^2} \tag{2}$$

where the rescaled variables are defined as $\bar{p} = p/p_*$, $\bar{T} = T/T_*$ and $\bar{v} = v/v_*$. Note, that a and b no longer appear in the equation of state. What is the significance of this?

e) The critical point of nitrogen gas is $T_* = 126°$ K and $p_* = 34$ bar (1 bar $= 10^5$ Pa.) Estimate its van der Waals constants a and b, and predict its density at the critical point.

Problem 3: **(6 points)**

Maxwell suggested replacing the "wiggle" of the van der Waals isotherm by a straight, horizontal line, as shown in the next figure.

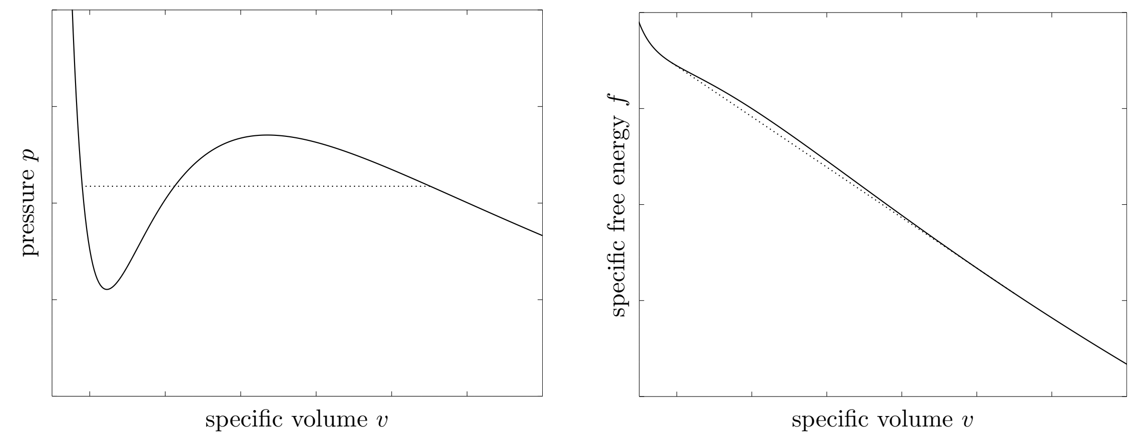

Figure 2: A typical isotherm for $T < T_*$: Left: in the (p, v) plane, Right: in the (f, v) plane. In both cases, the solid line represents the values obtained by directly using (1). The dotted line shows the Maxwell construction.

In this problem, we investigate why Maxwell thought it necessary to "correct" the van der Waals equation of state, and why he choose to modify it in this way.

a) Explain why the molar free energy f for a van der Waals gas below the critical temperature must resemble the right panel of Figure 2.

b) Explain why the solid curves between v_a and v_b will bever be observed. If the solid curves are replaced by the dotted ones, explain why the resulting curves could be observed.

c) In the (p, v) plane, the dotted line is chosen so that the areas A and B are equal:

$$p_{ab}(v_b - v_a) = \int_{v_a}^{v_b} p \, \mathrm{d}v. \tag{3}$$

In the (f, v) plane, the dotted line is chosen to make f convex. Show that these two formulations of the Maxwell construction are equivalent.

d) Explain why we would expect that $\mu(v_a, T, p_{ab}) = \mu(v_b, T, p_{ab})$ and show that the Maxwell construction satisfies thes relationship.

e) Equation (3) contains three unknowns: p_{ab}, v_a and v_b. Write down two more equations that one could use to uniquely determine the three unknowns (given that T is fixed - we are considering moving along an isotherm). What is the physical meaning of $p_{ab}(T)$?

f) Explain how you would construct an experiment to follow the isotherms in Figure 2. What would you observe for $v_a < v < v_b$?

Deliver your hand-written solutions at the beginning of the lecture on Friday, May 26th.