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| Problems set # 2 | **Physics 303**   September 9, 2014

1. Van der Waals equation of state for a non-ideal gas describing its transition to liquid has the form

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT,$$

where a describes attraction of the gas molecules and b describes the volume occupied by the molecules and thus excluded from their motion. *(i)* Plot isotherms of this gas for diferent T, setting $a = b = R = 1$. Verify that at high T isotherms are close to those for an ideal gas, but for lower T they become distorted. Show that below a critical temperature $T < T_C$ there is a local maximum and minimum of P. The transition between the two types of curves (that is where $T = T_C$) is a curve having an inflection point called the critical point (CP). This transition curve is known as the critical curve. *(ii)* Calculate the isothermal compressibility of the van der Waals gas in terms of (v, T). Obtain its high-temperature limit. What happens with it at the critical point? *(iii)* Find the critical point parameters using the analysis in *(i)* as a hint.

Solution: *(i)* See Fig. 1. Straightforward calculus analysis would determine the exact location of maxima and minima. *(ii)* Rewrite the compressibility as $\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = -\frac{1}{v}\left(\frac{\partial P}{\partial v}\right)_T^{-1}$ and solve the equation of state for P as $P = \frac{RT}{v-b} - \frac{a}{v^2}$. You can see that the b-term increases pressure whereas the a-term decreases pressure, as expected. Differentiating P you first find $\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$ that yields $\kappa_T = -\frac{1}{v}\frac{1}{2a/v^3 - RT/(v-b)^2} = \frac{(v-b)^2/v}{RT - 2a(v-b)/v^3}$. At high temperatures v becomes large, so you can neglect the terms with a and b to obtain $\kappa_T = v/(RT) = P^{-1}$, which is the result for an ideal gas. With lowering T, the volume decreases and the negative term in the denominator causes κ_T to diverge at the critical point. *(iii)* To find the critcal point use $\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$, that is $\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0$ and $\left(\frac{\partial^2 P}{\partial v^2}\right)_T = -\frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0$. Getting rid of the denominators, you obtain the following system of equations $RTv^3 = 2a(v-b)^2$ and $RTv^4 = 3a(v-b)^3$. Divide the second equation by the first one to get $v = \frac{3}{2}(v-b)$. Solving this equation you obtain the critical volume: $v_C = 3b$. After that you can obtain the critical temperature $RT_C = \frac{2a}{v_C^3}(v_C - b)^2 = \frac{8a}{27b}$. Finally, the critical pressure follows from the equation of state: $P_C = \frac{RT_C}{v_C - b} - \frac{a}{v_C^2} = \frac{a}{27b^2}$.

2. Using the Berthelot equation of state,

$$P = \frac{RT}{v - b} - \frac{a}{Tv^2},$$

show that $v_C = 3b$, $T_C = \sqrt{\frac{8a}{27bR}}$, and $P_C = \frac{1}{12b}\sqrt{\frac{2aR}{3b}}$. Compare the numerical value of $RT_C P_C^{-1} v_C^{-1}$ with the experimental values given in Table 1.

Solution: At the critical point $\left(\frac{\partial P}{\partial V}\right)_{CP} = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_{CP} = 0$. For the equation of state at hand, $\left(\frac{\partial P}{\partial V}\right) = -\frac{RT}{(v-b)^2} + \frac{2a}{Tv^3}$ and $\left(\frac{\partial^2 P}{\partial V^2}\right) = \frac{2RT}{(v-b)^3} - \frac{6a}{Tv^4}$. The condition at the critical point leads to
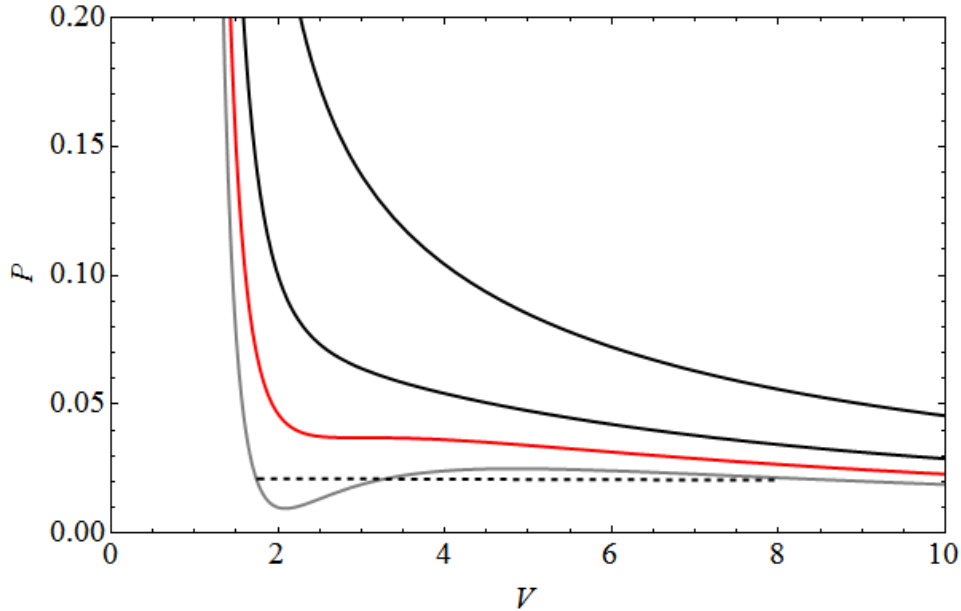
Figure 1: Isotherms of the van der Waals gas.

$\frac{RT_C}{(v_C-b)^2} = \frac{2a}{T_C v_C^3}$ and $\frac{2RT_C}{(v_C-b)^3} = \frac{6a}{T_C v_C^4}$. Solve the system of equations to obtain $v_C = 3b$, $T_C = \sqrt{\frac{8a}{27Rb}}$, which yield $P_C = \frac{RT_C}{v_c-b} - \frac{a}{T_C v_c^2} = \sqrt{\frac{aR}{216b^3}}$. The theoreticall value, $\frac{RT_C}{P_C v_C} = 2.67$, is always smaller than the experimental value for all the given gases.

3. Using the Dieterici equation of state,

$$P = \frac{RT}{v - b} \exp\left\{-\frac{a}{RTv}\right\},$$

show that $v_C = 2b$, $T_C = \frac{a}{4Rb}$, $P_C = \frac{a}{4e^2b^2}$, and find the numerical value of $RT_C P_C^{-1} v_C^{-1}$. How does this compare with the tabulated experimental values?

Solution: At the critical point $\left(\frac{\partial P}{\partial V}\right)_{CP} = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_{CP} = 0$. For the equation of state at hand $P = \frac{RT}{v-b}e^{-a/(RTv)}$, the partial derivatives read $\left(\frac{\partial P}{\partial V}\right) = e^{-a/(RTv)}\left[-\frac{RT}{(v-b)^2} + \frac{a}{(v-b)v^2}\right]$ and $\left(\frac{\partial^2 P}{\partial V^2}\right) = e^{-a/(RTv)}\left\{\frac{1}{v^2}\frac{a}{v-b}\left[\frac{a}{RTv^2} - \frac{1}{v-b}\right] + \frac{2RT}{(v-b)^3} - a\left[\frac{1}{v^2(v-b)^2} + \frac{2}{v^3(v-b)}\right]\right\}$. The condition at the critical point determine a system of equations. Solve the system to obtain $v_C = 2b$, $T_C = \frac{a}{4Rb}$. Substitute in the equation of state to obtain $P_C = \frac{RT_C}{v_C-b}e^{-a/(RT_C v_C)} = \frac{a}{4b^2e^2}$. The theoretical value of $\frac{RT_C}{P_C v_c} = 3.69$, which is greater than the experimental values of He, H_2, O_2, CO_2, but is less than that of H_2O.

4. (i) Making use of the triple product find the expansivity β of a substance obeying the Dieterici equation of state. (ii) At high temperature and high specific volumens (low densities) all gases approximate an ideal gas. Show that for large values of T and v, the expression for β obtained in (i) goes over to the corresponding equation for an ideal gas.

Substance	$RT_C P_C^{-1} v_C^{-1}$
He	3.06
H_2	3.27
O_2	3.42
CO_2	3.61
H_2O	4.29

Solution: *(i)* From the triple product you know that $\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial P}\right)_T$. For the Dieterici equation of state, these partial derivatives are given by: $\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b} e^{-a/(RTv)} \left(1 + \frac{a}{RTv}\right)$ and $\left(\frac{\partial v}{\partial P}\right)_T = \left(\frac{\partial P}{\partial v}\right)_T^{-1} = \left[\frac{RT}{v-b} e^{-a/(RTv)} \left(\frac{a}{RTv^2} - \frac{1}{v-b}\right)\right]^{-1}$. Finally, $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = -\frac{1}{v}\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial P}\right)_T = \frac{R+a/(vT)}{RvT/(v-b)-a/v}$. *(ii)* For large v and T, $v \gg b$ and $RvT \gg a$, the expression for β reduces to T^{-1} as expected in ideal gas.

5. Show that β and κ_T are infinite at the critical point.

Solution: On the one hand, $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1/V}{(\partial P/\partial V)_T}$. At the critical point $\left(\frac{\partial P}{\partial V}\right) = 0$ and hence $\kappa \to \infty$. On the other hand, $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ can be rewritten using the tripe product, $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$, as $\beta = -\frac{1}{V}\frac{1}{(\partial P/\partial V)_T}\frac{1}{(\partial T/\partial P)_V}$. At the critical point $\left(\frac{\partial P}{\partial V}\right) = 0$ and so $\beta \to \infty$.