# 5163, Homework Assignment 5
# due on Friday, 03/04/2022, at 6pm (to be uploaded to Canvas)

This homework set consists of four problems.

Problem 1:
In 1906, Berthelot proposed the following equation of state as an improvement of the ideal gas equation of state:

$$\left(P + \frac{a}{kTv^2}\right)(v - v_0) = kT. \tag{1}$$

Here, $a$ and $v_0$ are substance specific constants (they have to be determined for each substance) and $v$ is equal to $V/N$, with $N$ being the number of atoms or molecules in the substance. Let us consider a gas that satisfies Berthelot's equation of state as well as the additional condition that the internal energy $U$ approaches $5NkT/2$ in the $v \to \infty$ limit.
(a) Determine the Helmholtz free energy $A$ (your answer will depend on an undetermined constant).
(b) Determine the specific heat $C_V$ at constant volume,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \tag{2}$$

in terms of $T$ and $v$.

Problem 2:
In Problem 1, we determined the pressure and internal energy of a substance governed by Berthelot's equation of state, subject to the condition $U \to 5NkT/2$ for $v \to \infty$.
(a) What are the units of $a$ and $v_0$ that enter into Berthelot's equation of state? Use your result to rewrite the pressure and internal energy per particle as dimensionless quantities (denote the dimensionless pressure by $\tilde{P}$ and the dimensionless internal energy per particle by $\tilde{\epsilon}$).
Note: In the process, you will have to define a dimensionless volume $\tilde{v}$ and a dimensionless temperature $\tilde{\tau}$ (or more precisely, Boltzmann constant times temperature).
(b) Determine the critical dimensionless temperature $\tilde{\tau}_c$, which is obtained by enforcing

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{v}}\right)_T = 0 \tag{3}$$

and

$$\left(\frac{\partial^2 \tilde{P}}{\partial \tilde{v}^2}\right)_T = 0. \tag{4}$$

Explain how Eq. (3) relates to the isothermal compressibility. Explain whether or not

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{v}}\right)_T > 0 \tag{5}$$

and

$$\left(\frac{\partial \tilde{P}}{\partial \tilde{v}}\right)_T < 0 \tag{6}$$

are physical.
(c) Plot isotherms in a $\tilde{P}$ versus $\tilde{v}$ diagram. Include the equation of state for $\tilde{\tau} = \tilde{\tau}_c$, $\tilde{\tau} < \tilde{\tau}_c$, and $\tilde{\tau} > \tilde{\tau}_c$. Do you encounter negative $\tilde{P}$? Does this bother you?

Problem 3:
A gas consisting of $N$ identical classical particles is confined inside a cylinder of length $L = a - b$ and with volume $V = \pi R^2 L$, i.e., the particles' coordinates are restricted by $b < z < a$ and $x^2 + y^2 < R^2$. The particles do not interact with each other and the motion of a single particle is governed by the Hamiltonian $\mathcal{H} = \vec{p}^2/(2m) + Kz$, where $K$ is a constant. Let us assume that the gas is in equilibrium.
(a) Calculate the partition function of the gas.
(b) Determine the pressure $P_a$ of the gas on the wall at $z = a$.
(c) Determine the pressure $P_b$ of the gas on the wall at $z = b$.
(d) Compare the pressures $P_a$ and $P_b$ in the limit $KL \gg kT$. Explain.

Problem 4:
This problem investigates the properties of the van der Waals equation of state,

$$(v - b)\left(P + \frac{a}{v^2}\right) = kT, \tag{7}$$

where $a$ and $b$ are substance specific constants and $v = V/N$.
(a) Show that the van der Waals equation of state reduces to the ideal gas equation of state in the ultralow density limit and derive the leading-order correction to the ideal gas equation of state in the low density limit.
(b) For neon, the following holds:

$$b - \frac{a}{kT} \to 1.3 \times 10^{-5} \frac{\mathrm{m}^3}{\mathrm{mol}} \quad \text{for} \quad T \to \infty \tag{8}$$

and

$$b - \frac{a}{kT} \to 0 \quad \text{for} \quad T \to 125\ \mathrm{K}. \tag{9}$$

Using these relations, determine $a$ and $b$ for neon.
(c) Determine the critical volume $v_c$ and critical temperature $T_c$ for neon from the conditions

$$\left(\frac{\partial P}{\partial v}\right)_T = 0 \tag{10}$$

and

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0. \tag{11}$$

What is the critical pressure? Compare your results with the experimentally determined values of $T_c = 44.5$ K and $P_c = 26.9$ atm.