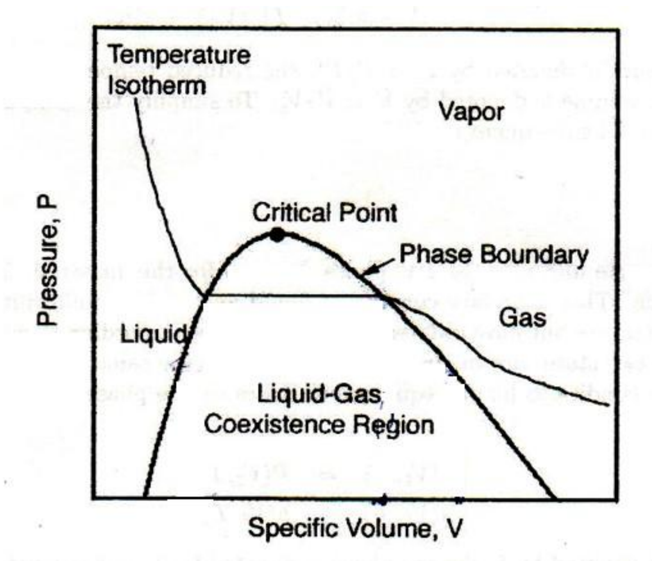
Amalgam – Coding event - Question 2.

The fields of phase stability for a pure material

The phase behavior of a pure material can be represented via a ***P-V*** diagram, where ***P*** is pressure and ***V*** is specific volume. A typical diagram is depicted below (please ignore the hand-drawn wiggles; all curves should be smooth).



Your task is to construct such a phase diagram which depicts the phase boundary and temperature isotherms for a material which obeys the Redlich-Kwong equation of state, namely:

$$\hat{P} = \frac{R\hat{T}}{\hat{V} - b} - \frac{a}{\hat{T}^{1/2}\,\hat{V}\,(\hat{V} + b)}$$

where $\hat{P}$ is the pressure, R is the ideal gas law constant, $\hat{V}$ is the specific volume, $\hat{T}$ is the absolute temperature, and a and b are constants for a given material. The critical point must satisfy the following conditions:

$$\left(\frac{\partial \hat{P}}{\partial \hat{V}}\right)_{T_c} = 0, \quad \text{and} \quad \left(\frac{\partial^2 \hat{P}}{\partial \hat{V}^2}\right)_{T_c} = 0.$$

where T_c denotes the critical temperature. For the Redlich-Kwong equation of state, it is relatively straightforward to show that the above requirements lead to:

$$a = \frac{\Omega_a R^2 T_c^{5/2}}{P_c},$$

$$b = \frac{\Omega_b R T_c}{P_c}.$$

where P_c denotes the critical pressure, V_c is the critical volume, and Ω_a and Ω_b are constants, with

$$\Omega_a = \frac{1}{9(2^{1/3} - 1)},$$

$$\Omega_b = \frac{2^{1/3} - 1}{3}.$$

With the above, we can rewrite the Redlich-Kwong equation in a dimensionless form, as follows:

$$\boxed{P(V,T) = \frac{3T}{V - 3\Omega_b} - \frac{9\Omega_a}{T^{1/2} V (V + 3\Omega_b)}} \qquad \textbf{(1)}$$

where $P = \widehat{P}/P_c$, $V = \widehat{V}/V_c$, and $T = \widehat{T}/T_c$ are the dimensionless pressure, specific volume, and temperature respectively.

Equations for plotting the phase boundaries

(1) For liquid-gas equilibrium at a particular temperature T, we should have

$$P(V_1, T) = P(V_2, T),$$

where liquid phase is denoted by **1** and the gas phase by **2**.

(2) The chemical potentials of the two phases should be equal at that particular temperature T:

$$\mu(V_1, T) = \mu(V_2, T).$$

Thus we have two equations in two unknowns. The unknowns are $\boldsymbol{V_1}$ and $\boldsymbol{V_2}$, and we assume that $\boldsymbol{T}$ is set to some value, so it is not an unknown. For the first equation (equality of pressures), we already have an equation of state, given by the boxed equation **(1)** above. For the equality of chemical potentials, we need to derive a usable algebraic form. Using the fundamental relations of thermodynamics, it is easy to show that:

$$\boldsymbol{\mu(V,T) = C(T) + \frac{3VT}{V - 3\Omega_b} - \frac{9\Omega_a}{T^{1/2}\,(V + 3\Omega_b)} - 3T\,ln(V - 3\Omega_b) - \frac{3\Omega_a}{T^{1/2}\Omega_b}\,ln\left(\frac{V + 3\Omega_b}{V}\right)} \quad \textbf{(2)}$$

where $\boldsymbol{C(T)}$ is an arbitrary function of $\boldsymbol{T}$.

Tasks

(a) Write down explicitly, the system of two nonlinear algebraic equations that you would solve for locating the phase boundaries in terms of $\boldsymbol{V_1}$ and $\boldsymbol{V_2}$, using the two boxed equations **(1)** and **(2)**.

(b) Come up with a program to solve these equations. Write your own code/script in MATLAB, Octave. You need to attach the program.
Wherever possible, comments in the code should explain the purpose of the statements, how it works, and its major variables/nomenclature.

(c) Run your code for multiple values of $\boldsymbol{T}$ and find out $\boldsymbol{V_1}$ and $\boldsymbol{V_2}$.

(d) Back substitute either $\boldsymbol{V_1}$ or $\boldsymbol{V_2}$ into the first boxed equation to find out the values of pressure at all temperatures. Now, you have all the data points to locate the phase envelope.

(e) Plot the temperature isotherms on the phase diagram, like the one shown on **Page 1**. Remember that for $\boldsymbol{T}$ < 1, the isotherms should be perfectly straight and horizontal through the two-phase coexistence region.