

## 0.1 Homework 4

### 0.1.1 Van der Waals equation

1. Derive for the dimensionless van der Waals equation of state from the original vdW equation  $P = \frac{RT}{v-b} - \frac{a}{v^2}$ .

The conditions for the critical point are

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

So compute the derivatives of the pressure  $P$ :

$$\begin{cases} \frac{\partial P}{\partial v} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}, \\ \frac{\partial^2 P}{\partial v^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4}. \end{cases}$$

At the critical point, let  $v = v_c$ ,  $P = P_c$ ,  $T = T_c$ , and we have the following equations:

$$\begin{cases} \frac{RT_c}{(v_c-b)^2} - \frac{2a}{v_c^3} = 0, \\ \frac{2RT_c}{(v_c-b)^3} - \frac{6a}{v_c^4} = 0. \end{cases} \Rightarrow \begin{cases} RT_c = \frac{2a(v_c-b)^2}{v_c^3}, \\ RT_c = \frac{3a(v_c-b)^3}{v_c^4}. \end{cases} \Rightarrow v_c = 3b$$

Since  $v_c$  has been determined, we can substitute it into the first equation to get:

$$RT_c = \frac{2a(3b-b)^2}{(3b)^3} = \frac{8a}{27b} \Rightarrow T_c = \frac{8a}{27Rb}$$

$$P_c = \frac{RT_c}{v_c-b} - \frac{a}{v_c^2} = \frac{a}{27b^2}.$$

Rescale the variables with the critical conditions:

$$P_r = \frac{P}{P_c}, \quad v_r = \frac{v}{v_c}, \quad T_r = \frac{T}{T_c}.$$

$$\Leftrightarrow P = P_r P_c = P_r \cdot \frac{a}{27b^2}, \quad v = v_r v_c = v_r \cdot 3b, \quad T = T_r T_c = T_r \cdot \frac{8a}{27Rb}.$$

So the van der Waals equation of state come to be

$$P_r \cdot \frac{a}{27b^2} = \frac{RT_r \cdot \frac{8a}{27Rb}}{v_r \cdot 3b - b} - \frac{a}{(v_r \cdot 3b)^2}$$

$$\Rightarrow P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}.$$

2. Plot typical curves  $P(v)$  at high and low temperature. In the derivation, one should identify the critical point. Show all your work.

*% Define the reduced volume range*

`v_r = linspace(0.5, 10, 1000);`

*% High temperature ( $T_r > 1$ , e.g.,  $T_r = 1.5$ )*

`T_r_high = 1.5;`

`P_r_high = 8 * T_r_high ./ (3 * v_r - 1) - 3 ./ (v_r.^2);`

*% Low temperature ( $T_r < 1$ , e.g.,  $T_r = 0.8$ )*

`T_r_low = 0.8;`

`P_r_low = 8 * T_r_low ./ (3 * v_r - 1) - 3 ./ (v_r.^2);`

*% Critical isotherm ( $T_r = 1$ )*

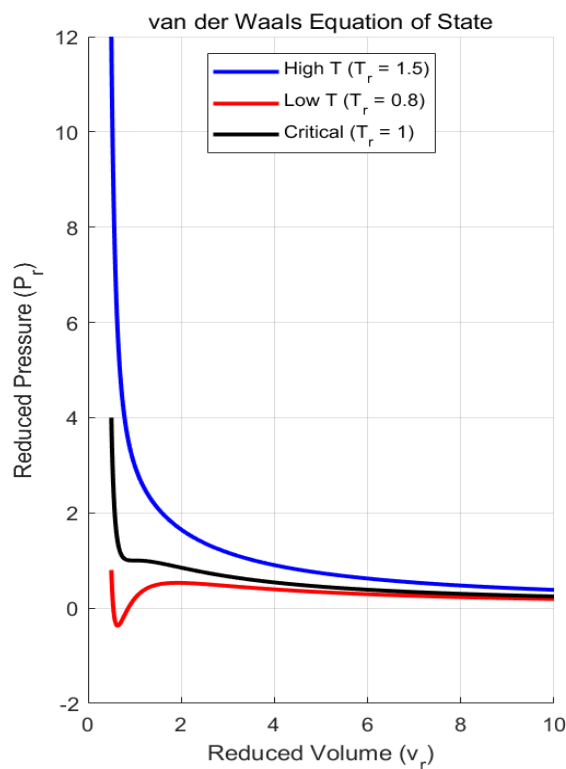
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T_r_critical = 1;
P_r_critical = 8 * T_r_critical ./ (3 * v_r - 1) - 3 ./ (v_r.^2);

% Plotting
figure;
hold on;
plot(v_r, P_r_high, 'b', 'LineWidth', 2, 'DisplayName', 'High T (T_r = 1.5)');
plot(v_r, P_r_low, 'r', 'LineWidth', 2, 'DisplayName', 'Low T (T_r = 0.8)');
plot(v_r, P_r_critical, 'k', 'LineWidth', 2, 'DisplayName', 'Critical (T_r = 1)');
xlabel('Reduced Volume (v_r)');
ylabel('Reduced Pressure (P_r)');
title('van der Waals Equation of State');
legend('Location', 'best');
grid on;
hold off;

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The figure is shown below:



## 0.1.2 Maxwell Equal Area Construction

**Derive for the Maxwell equal area construction.**

The van der Waals equation of state for a non-ideal gas is given by

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

The Maxwell construction replaces an unphysical "loop" with a horizontal line (Constant  $P$ ), representing liquid-vapor coexis-

tence. Conditions for phase equilibrium are:

$$P(T, V_g) = P(T, V_l) = P_{\text{sat}}, \quad V_{g/l}: \text{ the molar volume of gas/liquid phases.}$$

$$\mu_g(T, P) = \mu_l(T, P)$$

Since  $G = \mu N$  and  $dG = -SdT + VdP$ , we have:

$$\mu_g - \mu_l = \int_{V_l}^{V_g} \left( \frac{\partial \mu}{\partial V} \right)_T dV = \int_{V_l}^{V_g} v dP = 0$$

Since  $P$  is constant ( $P_{\text{sat}}$ ) along the coexistence line, we can write:

$$\int_{V_l}^{V_g} v dP = P_{\text{sat}}(V_g - V_l) - \int_{P_l}^{P_g} P dV = 0$$

And we know that  $P_l = P_g = P_{\text{sat}}$ , so this reduces to

$$\boxed{\int_{V_l}^{V_g} P dV = P_{\text{sat}}(V_g - V_l)},$$

which is the conclusion to be derived.

### 0.1.3 Virial Expansion

Assume that in the virial expansion

$$\frac{Pv}{kT} = 1 - \sum_{j=1}^{\infty} \frac{j}{j+1} \beta_j \left( \frac{\lambda^3}{v} \right)^j,$$

where  $\beta_j$  are the irreducible cluster integrals of the system, only terms with  $j = 1$  and  $j = 2$  are appreciable in the critical region.

#### 1. Determine the relationship between $\beta_1$ and $\beta_2$ at the critical point, and

Since only the first two terms are appreciable, we can write the virial expansion as:

$$\frac{Pv}{kT} \simeq 1 - \left( \frac{1}{2} \beta_1 \frac{\lambda^3}{v} + \frac{2}{3} \beta_2 \frac{\lambda^6}{v^2} \right) = 1 - \frac{\beta_1 \lambda^3}{2v} - \frac{2\beta_2 \lambda^6}{3v^2}.$$

Or we can write it as a pressure function  $P$  of variable  $v$ :

$$P = kT \left( v^{-1} - \frac{\beta_1 \lambda^3}{2} v^{-2} - \frac{2\beta_2 \lambda^6}{3} v^{-3} \right)$$

So list the derivatives of  $P$  with respect to  $v$ :

$$\frac{\partial P}{\partial v} = kT(-v^{-2} + \beta_1 \lambda^3 v^{-3} + 2\beta_2 \lambda^6 v^{-4})(=0),$$

$$\frac{\partial^2 P}{\partial v^2} = kT(2v^{-3} - 3\beta_1 \lambda^3 v^{-4} - 8\beta_2 \lambda^6 v^{-5})(=0),$$

which brings the critical point conditions:

$$-v_c^{-2} + \beta_1 \lambda^3 v_c^{-3} + 2\beta_2 \lambda^6 v_c^{-4} = 0,$$

$$2v_c^{-3} - 3\beta_1 \lambda^3 v_c^{-4} - 8\beta_2 \lambda^6 v_c^{-5} = 0.$$

We can rewrite the equations as

$$-v_c^2 + \beta_1 \lambda^3 v_c + 2\beta_2 \lambda^6 = 0, \quad (1)$$

$$2v_c^2 - 3\beta_1 \lambda^3 v_c - 8\beta_2 \lambda^6 = 0. \quad (2)$$

So the target is to eliminate terms like  $v_c$ . (1)×2+(2) gives

$$(2v_c^2 - 2v_c^2) = (3\beta_1\lambda^3v_c - 2\beta_1\lambda^3v_c) + (8\beta_2\lambda^6 - 4\beta_2\lambda^6)$$

$$\Rightarrow 0 = \beta_1\lambda^3v_c + 4\beta_2\lambda^6 \Rightarrow \boxed{\beta_1 = -\frac{4\beta_2\lambda^3}{v_c}}.$$

Substitute this into (1) gives:

$$v_c^2 = \left(-4\beta_2\frac{\lambda^3}{v_c}\right)\lambda^3v_c + 2\beta_2\lambda^6$$

$$\Rightarrow v_c^2 = -2\beta_2\lambda^6 \Rightarrow \boxed{v_c = \sqrt{-2\beta_2}\lambda^3}$$

This connects  $\beta_1$  and  $\beta_2$ :

$$\beta_1 = -\frac{4\beta_2\cancel{\lambda^3}}{\sqrt{-2\beta_2}\cancel{\lambda^3}} = 2\sqrt{-2\beta_2}.$$

So we have  $\boxed{\beta_1 = 2\sqrt{-2\beta_2}}$ .

2. **show that**  $\frac{kT_c}{P_c v_c} = 3$ .

From the previous problem, we have  $\beta_1 = \frac{2v_c}{\lambda^3}$  and  $\beta_2 = -\frac{v_c^2}{2\lambda^6}$ . Substituting these into the virial expansion gives:

$$\frac{P_c v_c}{kT_c} \simeq 1 - \frac{2v_c}{\lambda^3} \cdot \frac{\lambda^3}{2v_c} - \left(-\frac{v_c^2}{2\lambda^6}\right) \frac{2\lambda^6}{3v_c^2}$$

$$= 1 - 1 + \frac{1}{3} = \frac{1}{3}$$

So we have  $\boxed{\frac{kT_c}{P_c v_c} = 3}$