

PHYS 301

Thermodynamics and Statistical Mechanics

Homework Assignment 9

Due date: Monday April 20 2026 5pm, submitted on UNM Canvas

Question 1 (12 points).

Consider a van der Waals monoatomic gas of N particles of mass m in a volume V and at temperature T . Its equation of state is given by

$$\left(P + \frac{N^2 a}{V}\right) (V - Nb) = Nk_B T, \quad (1)$$

where a and b are constants that depends on the nature of the gas.

(a) Show that the entropy of this gas is given by

$$S = Nk_B \left[\ln \left(\frac{V - Nb}{\lambda_Q^3 N} \right) + \frac{5}{2} \right], \quad (2)$$

where $\lambda_Q = h/\sqrt{2\pi m k_B T}$.

(b) Show that the average energy of this gas is

$$\langle E \rangle = \frac{3}{2} Nk_B T - \frac{N^2 a}{V}. \quad (3)$$

(c) Consider the isotherms ($T = \text{constant}$ lines in the P versus V plane) of the van der Waals equation of state. There is a critical temperature T_c at which

$$\left. \frac{\partial P}{\partial V} \right|_{T=T_c} = 0, \quad \left. \frac{\partial^2 P}{\partial V^2} \right|_{T=T_c} = 0. \quad (4)$$

Compute T_c , as well as the corresponding pressure P_c and volume V_c .

(d) Rewrite the van der Waals equation of state in terms of the dimensionless variables

$$t \equiv T/T_c, \quad p \equiv P/P_c, \quad v \equiv V/V_c. \quad (5)$$

Note how the constants a and b disappear. In terms of these new variables, all gases look the same. This is known as the *law of the corresponding states*.

(e) Compute the so-called *universal compressibility ratio*

$$\frac{P_c V_c}{Nk_B T_c} \quad (6)$$

for the van der Waals gas. Experimental values for real gases range from around 0.28 to 0.3. How does the van der Waals prediction compare with these numbers?

Question 2 (5 points).

Consider the Dieterici equation of state for a gas of N particles in volume V and temperature T

$$P = \frac{Nk_{\text{B}}T}{V - Nb} e^{-\frac{aN}{V k_{\text{B}}T}}, \quad (7)$$

where a and b are constants.

- (a) Compute the temperature, pressure, and volume T_c , P_c and V_c at the critical point.
- (b) Compute the compressibility ratio $(P_c V_c)/(N k_{\text{B}} T_c)$ for this gas. Is this number closer to the experimentally measured values mentioned in Question 1(e)? Can you explain why that is?
Hint: consider how the van der Waals equation of state is a limiting case of the Dieterici one.

Question 3 (3 points).

Consider the Clausius-Clapeyron equation for a first-order phase transition between a liquid and a gas phase

$$\frac{dP}{dT} = \frac{L}{T(v_{\text{gas}} - v_{\text{liquid}})}, \quad (8)$$

where L is the specific latent heat, and $v \equiv V/N$. Under the assumption that L is constant, $v_{\text{gas}} \gg v_{\text{liquid}}$, and $PV = Nk_{\text{B}}T$, solve the above equation to determine the shape of the liquid-gas interface line in the P versus T phase diagram.