

Please encircle the questions you have solved and are able to present/discuss in class.

3.1 (a) 3.1 (b) 3.1(c) 3.2(d) 3.2(e) 3.2(f)

Problem 3.1 (5 points)

Consider a system described by the following canonical partition function:

$$Z = \frac{1}{N!} \left(\frac{V - Nb}{N\lambda^3} \right)^N \exp(aN^2/k_B VT). \quad (1)$$

Here N is the number of particles, V is the volume, a, b are real constants, $\lambda = \sqrt{2\pi\hbar^2\beta/m}$ is the de Broglie thermal wavelength and k_B is the Boltzmann constant.

- (a) Find the equation of state $P(T, v)$ where $v = V/N$ is the volume per particle.

Hint: To obtain the equation of state, first evaluate the free energy. **(1 point)**

- (b) Compute the critical point $C = (P_c, v_c, T_c)$ of the liquid-gas phase transition, with $P_c = P(T_c, v_c)$. Plot the pressure $P(T; v)$ as a function of v for different fixed values of T . These curves are the so-called isothermal curves. How do the isothermal curves for $T < T_c$ differ from the ones for $T > T_c$?

Express the reduced pressure $\bar{P} = (P - P_c)/P_c$ in terms of the order parameter $\eta = v_c/v - 1$ and the reduced temperature $\tau = (T - T_c)/T_c$. **(2 points)**

Hint: The critical point $C = (P_c, v_c, T_c)$ is given by the inflection point of the equation of state $P(T, v)$ and it is therefore given by the solution of the following system of equations

$$\left. \frac{\partial P(T, v)}{\partial v} \right|_C = 0, \quad \text{and} \quad \left. \frac{\partial^2 P(T, v)}{\partial v^2} \right|_C = 0. \quad (2)$$

- (c) Calculate the critical exponents: $(\alpha, \beta, \gamma, \delta)$. **(2 points)**

Hint: Remember the definitions of the critical exponents. For example, given the order parameter η , the critical exponent β is defined by $\eta \sim (T_c - T)^\beta$ and the exponent α is defined as

$$C \sim (T - T_c)^{-\alpha}. \quad (3)$$

In the previous equation C is the heat capacity at constant volume of the system, which can be found from Z in Eq. (1) as

$$C = \frac{\partial \langle E \rangle}{\partial T}, \quad (4)$$

with $\langle E \rangle$ the mean energy.

Hint: You may make use of the following relations among the critical exponents (which will be derived in the lecture at a later stage)

$$\begin{aligned} \alpha + 2\beta + \gamma &= 2, \\ \alpha + \beta\delta + \beta &= 2. \end{aligned} \quad (5)$$

Problem 3.2 (5 points)

Consider the *Dietrici equation of state*, which provides a phenomenological description of a certain class of real gases:

$$P(V - b) = k_B T \exp(-a/k_B TV), \quad (6)$$

where V is the volume, P is the pressure, T the temperature, a, b are phenomenological real parameters and k_B the Boltzmann constant.

- (d) Evaluate the critical constants P_c , V_c , and T_c of the given system in terms of the parameters a and b , and show that the quantity $k_B T_c / P_c V_c = e^2/2 \approx 3.695$. **(2 points)**

- (e) Demonstrate that, for all values of P and for $T \geq T_c$, the Dietrici equation yields to a unique value of V .
Hint: Study the sign of the function $(\frac{\partial P}{\partial V})$ for $T \geq T_c$. **(2 points)**
- (f) Demonstrate that for $T < T_c$, there are three possible values of V , for a given value of P , and the critical volume V_c is always intermediate between the largest and the smallest of the three volumes.
Hint: Study the sign of the function $P(V, T)$, for fixed $T < T_c$ as a function of V , and find the intervals where the function itself is increasing with respect to V . **(1 point)**