

## Problem set 1 – Liquids

### Problem 1

Consider a process in which  $n$  moles of a perfect mono-atomic gas expands isothermally and reversibly from volume  $V_1$  to volume  $V_2 = 2V_1$ .

- What is the change in internal energy for this process?
- Starting from the thermodynamic definition of entropy  $dS = \frac{dq_{rev}}{T}$  show that the entropy change  $\Delta S$  for this reversible expansion is given by

$$\Delta S = nR \ln 2.$$

- Write the answer to part b) in the form of Boltzmann's statistical definition of entropy,  $S = k_B \ln \Omega$ , hence, show that  $\frac{\Omega_2}{\Omega_1} = 2^N$ . How does the number of possible ways to realise a given configuration change due to the expansion?
- From the fundamental equation for the Helmholtz free energy, derive the following Maxwell-relation

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial p}{\partial T}\right)_{V,n}.$$

and use this to calculate the entropy change for an isothermal expansion of a perfect monatomic gas from volume  $V_1$  to volume  $V_2 = 2V_1$  (cf part b).

### Problem 2

- Starting from the Gibbs-Duhem equation,  $d\mu = -S_m dT + V_m dP$ , derive the Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}.$$

- Starting from the Clapeyron equation, clearly stating any approximations, derive the Clausius-Clapeyron equation for the vapour pressure of a liquid

$$\frac{d \ln p}{dT} = \frac{\Delta_{vap} H}{RT^2}.$$

- The enthalpy of vaporization of water is  $44.0 \text{ kJ mol}^{-1}$ . Estimate the vapour pressure of water at  $120 \text{ }^\circ\text{C}$ .
- Show that the Clapeyron equation for an equilibrium between a solid and its liquid is given by

$$p_2 - p_1 = \frac{\Delta_{fus} H}{\Delta_{fus} V} \ln \frac{T_2}{T_1}.$$

The enthalpy of fusion (melting) is  $6.01 \text{ kJ mol}^{-1}$ , the vapour pressure at the triple point is  $533.29 \text{ Pa}$  and the mass densities of ice and water at  $0^\circ\text{C}$  are  $0.917 \text{ g cm}^{-3}$  and  $1.0 \text{ g cm}^{-3}$  respectively. The molar mass of water is  $18 \text{ g mol}^{-1}$ .

- Calculate the difference between the melting point of ice at  $1 \text{ atm}$  pressure and at the temperature of the triple point of water and comment on the small value you (should) obtain.

### Problem 3

The Van der Waals equation of state for one mole ( $n = 1$ ) is given by

$$p = \frac{RT}{V - b} - \frac{a}{V^2}.$$

- a) Explain the physical significance of the Van der Waals parameters  $a$  and  $b$ .

The critical point is defined by the conditions

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0.$$

- b) Apply the above conditions to the Van der Waals equation state to find the critical volume  $V_c = 3b$ , temperature  $T_c = \frac{8a}{27Rb}$  and pressure  $p_c = \frac{a}{27b^2}$ .
- c) Due to intermolecular interactions carbon dioxide cannot be treated as a perfect gas, but does obey the Van der Waals equation. Given that  $a = 0.361 \text{ Jm}^3\text{mol}^{-2}$  and  $b = 42.9 \cdot 10^{-6} \text{ m}^3\text{mol}^{-1}$  for  $\text{CO}_2$ , calculate the  $V_c$ ,  $T_c$  and  $p_c$  for carbon dioxide. How does it compare to the actual critical temperature (304.2 K) and critical pressure (72.9 atm) of  $\text{CO}_2$ ?

The Van der Waals equation of state can also be written in terms of a virial expansion (for  $n = 1$  mole):

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \approx \frac{RT}{V} \left[ 1 + \left(b - \frac{a}{RT}\right) \frac{1}{V} + \dots \right].$$

- d) Calculate the Boyle temperature and explain why the Boyle temperature is generally higher than the critical temperature for a given gas.

### Problem 4

- a) Explain briefly what is meant by a canonical ensemble, and why it is a useful concept in statistical mechanics.
- b) State how the internal energy ( $U$ ) and the Helmholtz free energy ( $A$ ) are related to the canonical partition function  $Q \equiv Q(N, V, T)$ .
- c) The canonical partition function for an interacting gas is given approximately by

$$Q = \frac{1}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} (V - Nb)^N \exp \left[ \frac{aN^2}{V k_B T} \right]$$

where  $a$  and  $b$  are positive constants.

Show that  $p = k_B T (\partial \ln Q / \partial V)_{N, T}$  and, hence, obtain an expression for the pressure of the gas. Comment on your result.

- d) Show that the internal energy per atom is given by

$$\frac{U}{N} = \frac{3}{2} k_B T - a \frac{N}{V}.$$

and comment on the physical interpretation of the fact that this result does not depend upon  $b$ .

## Problem 5

- a) Show that the molecular partition function for a harmonic oscillator, for the case that the zero-point energy of the oscillator has been defined as zero, is given by

$$q_{vib} = \left(1 - e^{-h\nu/k_B T}\right)^{-1},$$

where the  $\nu$  is the vibrational frequency (in  $\text{s}^{-1}$ ). Note that  $1 + x + x^2 + \dots = (1 - x)^{-1}$ .

- b) The Einstein model of a solid comprises of  $N$  atoms free to undergo independent harmonic vibrational motion along the  $x$ ,  $y$  and  $z$  directions with the same Einstein frequency  $\nu_E$ . Show that the Einstein model of such a 3D solid with  $N$  atoms yields the following expression for internal energy

$$U(T) = 3Nh\nu_E \left(e^{h\nu_E/k_B T} - 1\right)^{-1}.$$

- c) Obtain an expression for the molar heat capacity of the solid at constant volume,  $C_V = (\partial U/\partial T)_V$ , and show that, if written in terms of the Einstein temperature  $\theta_E = h\nu_E/k_B$ , the following result is obtained

$$C_V(T) = 3Nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad \left[ = 3Nk_B \left(\frac{\theta_E}{T}\right)^2 \frac{e^{-\theta_E/T}}{(1 - e^{-\theta_E/T})^2} \right].$$

Note that this is another example of the *Law of Corresponding States*: if plotted as a function of the reduced temperature,  $T/\theta_E$ , the heat capacity  $C_V$  of various crystals will superimpose, just as we have seen in lecture 1 for the Van der Waals equation of state.

## Problem 6

A perfect monatomic gas in thermal equilibrium occupies a vertical cylinder of height  $h$  and cross-sectional area  $A$ , in a uniform gravitational field with characteristic acceleration  $g$ .

- a) Find an expression for the classical molecular partition function of the gas. Note that the potential energy for a gas molecule equals  $mgz$ .
- b) Show that in the limit of  $mg h/k_B T$  becoming very small (i.e. in the limit of no gravity), the classical molecular partition function of a perfect gas is recovered.
- c) Estimate the height  $h$  at which this simplification breaks down for xenon.

Note that

$$\int_{-\infty}^{\infty} \exp(-\alpha x^2) dx = \sqrt{\frac{\pi}{\alpha}}$$