Thermal Physics II – Solutions for Problem Sheet 1

1. Consequences of the Third Law of Thermodynamics

- Start:

$$c_p - c_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p$$

- Take $(\partial U / \partial V)_T$ from first law: $dU = TdS - pdV$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - p$$

  Note that $(\partial U / \partial V)_S = -p$ ONLY holds if the entropy is being kept constant, NOT if the volume is kept constant!

- $$c_p - c_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p$$

- In the limit $T \to 0$, the entropy S is only a function of the temperature. Hence, we have

$$\lim_{T \to 0} \left(\frac{\partial S}{\partial V} \right)_T = 0$$

- This means that

$$\lim_{T \to 0} (c_p - c_V) = T \times 0 \qquad \text{or} \qquad \lim_{T \to 0} \frac{c_p - c_V}{T} = 0$$

This means that the difference of the heat capacities at constant volume and constant pressure decays faster than the temperature if $T \to 0$.

Of course, it follows directly from the relation above that

$$\lim_{T \to 0} (c_p - c_V) = 0\,,$$

which is a much weaker restriction. As c_p approaches zero in the limit $T \to 0$, the heat capacity at constant volume, C_V, must do the same.

2. Maxwell Relation

- Start from first law: $dU = TdS - pdV + \mu dN$
- Then the first derivatives are

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T\,, \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -p\,, \qquad \left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$$

- The mixed derivatives of U must be equal as the internal energy is a total differential. Hence, we have

$$\left(\frac{\partial}{\partial N}\left(\frac{\partial U}{\partial S}\right)_{V,N}\right)_{S,V} = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial N}\right)_{S,V}\right)_{V,N}$$

- Now we insert the first derivatives from above (the first on the left side, the last on the right side) and obtain as required

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

3. Stability of the Equilibrium

- We start from the fundamental law of thermodynamics:

$$dU = TdS - pdV \qquad \text{or} \qquad dS = \frac{1}{T}\Big[dU + pdV\Big]\,.$$

- Now we take into account that entropy, internal energy and volume are extensive quantities (T and p can be different in both subsystems):

$$dS = dS_1 + dS_2 = \frac{1}{T_1}\Big[dU_1 + p_1 dV_1\Big] + \frac{1}{T_2}\Big[dU_2 + p_2 dV_2\Big]\,.$$

- Total internal energy and total volume are conserve (we only allow energy transfer *between* the two subsystems and replacement of one gas with the other). This means $dU_1 = -dU_2$ and $dV_1 = -dV_2$. We then have

$$dS = dS_1 + dS_2 = \Big[\frac{1}{T_1} - \frac{1}{T_2}\Big]dU_1 + \Big[\frac{p_2}{T_1} - \frac{p_2}{T_2}\Big]dV_1$$

- In equilibrium, the entropy reaches its maximum and we find

$$\left(\frac{\partial S}{\partial U_1}\right)_{V_1} = \Big[\frac{1}{T_1} - \frac{1}{T_2}\Big] = 0 \quad \text{and} \quad \left(\frac{\partial S}{\partial V_1}\right)_{U_1} = \Big[\frac{p_2}{T_1} - \frac{p_2}{T_2}\Big] = 0$$

These conditions can only be fulfilled if $T_1 = T_2$ and $p_1 = p_2$ as required.