Thermal Physics, Autumn 2016 CMI
Problem set 8
Due by the beginning of lecture on Wednesday Nov 2, 2016
Thermodynamic potentials, Clapeyron Equation.

1. $\langle \mathbf{5} \rangle$ We used extensivity of internal energy to derive the Gibbs-Duhem relation (in the so-called energy representation)

$$d\mu = \frac{V}{N} dp - \frac{S}{N} dT. \tag{1}$$

Use extensivity to obtain another version of the Gibbs-Duhem relation (in the so-called entropy representation)

$$d\left(\frac{\mu}{T}\right) = \frac{V}{N} d\left(\frac{p}{T}\right) + \frac{U}{N} d\left(\frac{1}{T}\right) \tag{2}$$

2. $\langle \mathbf{6} \rangle$ Let use the Gibbs free energy to re-derive the Clapeyron equation for the slope of the coexistence curve $p(T)$ in a p-T diagram for a 1st order liquid to vapour transition. We argued that the condition of phase equilibrium implied that the specific Gibbs free energy is an extremum. Show that if gas is isothermally compressed at temperature T and constant vapour pressure $p(T)$, then

$$g_g - g_l = (u_g - u_l) - T(s_g - s_l) + p(v_g - v_l) = 0. \tag{3}$$

Here the subscripts refer to gas and liquid while g, u, s, v are the specific Gibbs free energy, internal energy, entropy and volume. Use this equation and the 1st law to derive the Clapeyron equation

$$\frac{dp}{dT} = \frac{\lambda(T)}{T(v_g - v_l)} \tag{4}$$

where $\lambda(T)$ is the latent heat of vapourization.