Foundations of Physics 2B/3C 2019-2020

Thermodynamics – Workshop 4 Problems

Week Commencing 4th November

1. Manipulation of thermodynamic differential relations

This problem considers applications of thermodynamic relations and uses calculus to derive expressions for some system properties.

a) The Helmholtz function is defined by $F = U - TS$. Write down both forms of its total differential and identify which functions of state the partial derivatives correspond to. Using your result or otherwise, prove the following two thermodynamic relations (don't forget the product rule for differentiation!)

$$U = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial\left({}^{F}/_{T}\right)}{\partial T}\right)_V.$$

Hence show that the heat capacity at constant volume can be described via

$$C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V.$$

b) By considering the volume as a function of temperature and pressure, $V = V(T, P)$, derive the following relation

$$\frac{dV}{V} = \beta_p dT - \kappa_T dp,$$

where $\beta_p = \frac{1}{V}(\partial V/\partial T)_p$ is the isobaric expansivity and $\kappa_T = -\frac{1}{V}(\partial V/\partial p)_T$ is the isothermal compressibility. The above two parameters can be defined in terms of thermodynamic functions of state as $\beta_p = 3aT^3/V$ and $\kappa_T = b/V$ for some particular material, where a and b are constants.

i) Use this information find the equation of state of the material in question via integration of the above relationship, i.e.) $V = V(T, p)$;

ii) Determine the volume change if the system moves between the thermodynamic states (p_1, T_1) and (p_2, T_2).