**DEPARTMENT OF PHYSICS**
**INDIAN INSTITUTE OF TECHNOLOGY, MADRAS**

**PH5080 Physics** **Problem Set 4** **12.2.2022**

1. (a) Show that the extensivity of entropy defined by the condition

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \ ,$$

is equivalent to the partial differential equation

$$U \frac{\partial S}{\partial U} + V \frac{\partial S}{\partial V} + N \frac{\partial S}{\partial N} = S \ .$$

(b) Hence prove the Euler relation: $U = TS - PV + \mu N$ for a single-component ideal gas.

2. In thermodynamics, Maxwell's relations follow from exchanging the order of differentiation in the second derivative of the thermodynamic potential. For instance, consider

$$\frac{\partial^2 U}{\partial V \partial N} = \frac{\partial^2 U}{\partial N \partial V} \ .$$

The second law then implies

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

Obtain the three Maxwell relations that follow by considering the three distinct second derivatives of the Helmholtz Free Energy.

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

3. **The Maxwellian distribution of velocities in a gas:** Consider an ideal gas in contact with a heat bath at temperature $T$. The probability that the molecule has a velocity in the range $(\mathbf{v}, \mathbf{v} + d\mathbf{v})$:

$$P(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left[-\frac{m}{2k_B T}(v_x^2 + v_y^2 + v_z^2)\right] \ dv_x dv_y dv_z \quad .$$

This is the **Maxwellian distribution** of velocities. Observe that the probability is *a Gaussian in each component of* $\mathbf{v}$, with zero mean and variance $k_B T/m$. The standard deviation in each component is thus proportional to $T^{1/2}$.

(a) Let $p(v)$ be the probability that the *speed* of the particle lies between $v$ and $v + dv$. Obtain an expression for $p(v)$, and sketch $p(v)$ as a function of $v$.

(b) Hence calculate (i) the mean speed; (ii) the most probable speed; (iii) the r.m.s. speed.

(c) Let $\langle v \rangle$ and $\langle 1/v \rangle$ denote the mean values of $v$ and $1/v$ respectively. Show that $\langle v \rangle \langle 1/v \rangle$ is *greater* than unity. Can you show this without calculating the averages concerned, on general grounds?

(d) Calculate the mean value of $|v_x|$, the *magnitude* of the $x$-component of the velocity of the molecule.