IISER Mohali

[Session 2018-19, Even Semester]

PHY 304 (Statistical Mechanics)

Problem Set 01: Review of Thermodynamics

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1. Consider the differential
$$(x^2 - y^2)dx + xdy \equiv đf$$
   (a) Verify, if $đf$ is an exact differential.
   (b) Is $dg = đf/x^2$ an exact differential ?

2. Show that for a system undergoing isoentropic change at constant pressure, $\Delta H \leq 0$.

3. Show that for a thermodynamic system whose state is defined by the parameters T and V,
$$\left.\frac{\partial U}{\partial V}\right|_T = T\left.\frac{\partial p}{\partial T}\right|_V - p$$
   where, $U(T, V)$ is the internal energy of the system.
   (a) Assuming heat capacity (C_V) of a real gas to be independent of temperature, derive
$$U(T, V) = C_V T - \frac{a}{V} + \text{constant}.$$
   Interpret this result as V increases and provide physical explanation.
   (b) What would you conclude for an ideal gas ?

4. Show that for an ideal gas with d degrees of freedom undergoing adiabatic expansion, the relation between T and V is given by,
$$V^{\gamma-1}T = \text{constant},$$
   where, $\gamma = \frac{d+2}{d}$ is called adiabatic expansion index.

5. Derive following TdS equations:
$$\begin{aligned} TdS &= C_V dT + \frac{\alpha T}{\kappa_T} dV \\ &= C_P dT - \alpha T V dP, \end{aligned}$$
   where, $\alpha = 1/V(\partial V/\partial T)_P$ is known as coefficient of thermal expansion and $\kappa_T = -1/V(\partial V/\partial P)_T$ is called isothermal compressibility. Note that the quantities on the right hand side are experimentally accessible. Further, show that
   (a) $C_P - C_V = \frac{TV\alpha^2}{\kappa_T}$

(b) $\frac{\kappa_T}{\kappa_S} = \frac{C_P}{C_V} = \gamma$.

$\kappa_S = -1/V(\partial V/\partial P)_S$ is called adiabatic compressibility.

6. *Curie's Law* states that in a paramagnetic material the magnetic susceptibility $\chi \propto 1/T$. Argue that it is not consistent with the Third law of thermodynamics.

7. Prove that the conditions for thermodynamic stability implies, $\kappa_T \geq \kappa_S \geq 0$.

8. If two out of there variables x, y and z are independent, show that

$$\frac{\partial x}{\partial y}\bigg|_z \frac{\partial y}{\partial z}\bigg|_x \frac{\partial z}{\partial x}\bigg|_y = -1.$$

9. Show that the stability conditions following the *maximum entropy principle* are given by,

$$\frac{\partial^2 S}{\partial X_i^2} \leq 0; \quad \frac{\partial^2 S}{\partial X_i^2}\frac{\partial^2 S}{\partial X_j^2} - \Big(\frac{\partial^2 S}{\partial X_i \partial X_j}\Big)^2 \geq 0,$$

where X_i is an extensive variable of state.

10. Derive *Gibbs-Duhem relation* taking $S = S(U, V, N)$ as fundamental relation of Thermodynamics. Write down the equations of state corresponding to this fundamental relation.

11. The Jacobian of functions $y_1(x_1, x_2)$ and $y_2(x_1, x_2)$ is defined as,

$$J(x_1, x_2) = \frac{\partial(y_1, y_2)}{\partial(x_1, x_2)} = \begin{vmatrix} \frac{\partial y_1}{\partial x_1} & \frac{\partial y_1}{\partial x_2} \\ \frac{\partial y_2}{\partial x_1} & \frac{\partial y_2}{\partial x_2} \end{vmatrix}$$

This can be easily extended for m functions and m variables. Show that,

(a) $\frac{\partial(x_1,x_2)}{\partial(y_1,y_2)} = 1/\frac{\partial(y_1,y_2)}{\partial(x_1,x_2)}$

(b) $\frac{\partial(y_1,x_2)}{\partial(x_1,x_2)} = \left(\frac{\partial y_1}{\partial x_1}\right)_{x_2}$

(c) $\frac{\partial(y_1,y_2)}{\partial(x_1,x_2)} = \frac{\partial(y_1,y_2)}{\partial(z_1,z_2)}\frac{\partial(z_1,z_2)}{\partial(x_1,x_2)}$

12. The Grand potential $\Phi_G(T, V, \mu)$ can be obtained from $U(S, V, N)$ via Legendre Tranformation given by

$$\Phi_G = U - TS - \mu N.$$

Show that the heat capacity at constant volume $C_V = T(\partial S/\partial T)_{V,N}$ can be expressed as

$$C_V = T\Big(\frac{\partial S}{\partial T}\Big)_{V,\mu} - T\Big(\frac{\partial N}{\partial T}\Big)^2_{V,\mu}\Big/\Big(\frac{\partial N}{\partial \mu}\Big)_{V,T}$$