Indian Institute of Science Education and Research, Trivandrum

PHY-321 **Stat-Mech problem set 1** **13.1.2015**

Note: Deadline: 22 January 2015 (after the Stat-Mech Class)

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1. Compressibility of a system κ is defined to be the ratio of the fractional change of volume of a system to the applied pressure which causes that change. It is defined as

$$\kappa_Y = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{Y,N} \qquad (1)$$

where Y is the quantity held fixed during the application of the pressure and N is the number of particles. For example, Y can be temperature, in which case we obtain the isothermal compressibility or if it is entropy, this means isoentropic or adiabatic compressibility.

The coefficient of thermal expansion, α_P is defined to be the fractional change of volume per unit change of temperature, i. e.,

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \qquad (2)$$

(a) Show that, for an ideal gas

$$\kappa_T = \frac{1}{P}\,; \qquad \alpha_P = \frac{1}{T} \qquad (3)$$

(b) Show/verify that for a general system

$$\left(\frac{\partial C_P}{\partial P}\right) = -T\,V\left[\alpha_P^2 + \left(\frac{\partial \alpha_P}{\partial T}\right)_P\right] \qquad (4)$$

(c) Use the above expression and the ideal gas equation of state, show that

$$\left(\frac{\partial C_P}{\partial P}\right)_{T,N} = 0 \qquad (5)$$

2. Using the definition of specific heat capacities:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}\,;\ C_P = \left(\frac{\partial H}{\partial T}\right)_{P,N} \qquad (6)$$

For a general thermodynamic system, show that

(a)
$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}$$
(b)
$$C_P - C_V = \frac{T\,V\,\alpha_P^2}{\kappa_T}$$
(c) Using the above two relations, show that
$$\kappa_T - \kappa_S = \frac{TV\alpha_P^2}{C_P} \tag{7}$$

3. As was discussed in the class, entropy is maximum for an isolated system in equilibrium. Entropy and internal energy satisfy the following conditions:
$$d^2S \le 0\,;\ d^2U \ge 0 \tag{8}$$
These are called stability conditions for a system to be in equilibrium. The above condition is called concavity (convexity) property of entropy (internal energy). The above condition on internal energy leads to
$$\left(\frac{\partial T}{\partial S}\right)_V (dS)^2 + 2\left(\frac{\partial T}{\partial V}\right)_S dS\,dV - \left(\frac{\partial P}{\partial V}\right)_S (dV)^2 \ge 0 \tag{9}$$
Use this condition to show that
(a) $C_V \ge 0$
(b) $\kappa_S \ge 0$, $\kappa_T \ge 0$
(c) $C_P \ge C_V$

4. The van der Waals equation of state is given by
$$\left(P + \frac{a}{v^2}\right)(v - b) = k_B\,T \tag{10}$$
where $v = V/N$. Show that this equation violates the stability condition $\kappa_T \ge 0$ for some values of (P, V).

5. **Gibbs-Dunhem relation** Using Euler relation
$$U = T\,S - P\,V + \mu\,N \tag{11}$$
and the first-law of thermodynamics
$$dU = T\,dS - P\,dV + \mu\,dN \tag{12}$$

(a) obtain the following Gibbs-Dunhem relations

$$S\,dT - V\,dP + N\,d\mu = 0 \tag{13}$$

$$U\,d\left(\frac{1}{T}\right) + V\,d\left(\frac{P}{T}\right) - N\,d\left(\frac{\mu}{T}\right) = 0 \tag{14}$$

(b) Using the equations of state of the ideal gas and relation (**??**)

$$P\,V = N k_{_B} T \qquad U = \frac{3}{2} N\,k_{_B}\,T \tag{15}$$

show that the entropy of ideal gas is

$$S = N\,k_{_B}\left[\ln\left(\frac{U^{3/2}V}{N^{5/2}}\right) + \text{constant}\right] \tag{16}$$