Indian Institute of Science Education and Research, Trivandrum

PHY-221 **Stat-Mech Mid sem 1** **4.02.2015**

Instructions

1. This is a closed book exam. **Total of 20 points.**
2. **You are expected to answer all the 4 problems.** All problems carry equal points (5 points each).
3. Be clear; Be specific; Be neat.
4. Useful formulae are given at the end of the last question.

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1. Using Maxwell's relations, show that

   (a)
   $$\left(\frac{\partial H}{\partial T}\right)_V = C_P\left(1 - \frac{\beta\,\mu}{\kappa}\right) \qquad [2.5 \text{ points}]$$

   (b)
   $$\left(\frac{\partial U}{\partial P}\right)_T = V\left(\kappa P - \beta T\right) \qquad [2.5 \text{ points}]$$

   where C_P is specific heat at constant pressure

   $$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{is volume expansion coefficient}$$
   $$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{is isothermal compressibility}$$
   $$\mu = \left(\frac{\partial T}{\partial P}\right)_H \quad \text{is Joule Thompson coefficient}$$

2. (a) Given that the internal energy U for some system in thermodynamic equilibrium is
   $$U(S,V) = \frac{A\,S^3}{V}$$
   where A is a constant, S and V are entropy and volume, respectively. Determine $H(S,P)$, $F(T,V)$, and $G(T,P)$. [3 points]

(b) Suppose it is found experimentally for a solid that [2 points]

$$\left(\frac{\partial V}{\partial T}\right)_P = a + b\,P + c\,P^2$$

for pressures in the interval $P_1 < P < P_2$. Note that a, b, and c are constants. How much will the entropy increase when the solid is compressed from a pressure P_1 to P_2 at constant temperature T?

3. **Ideal gas law derived from the lattice model**

   Let us assume that gas particles can be modelled as a lattice. There are M lattice sites per unit volume V.

   Imagine gas to be composed to N spherical balls that are free to occupy one of these M lattice sites. [Note that $M > N$, i.e. the number of lattice sites are larger than the number of gas particles.]

   (a) Calculate the number of distinguishable arrangements (Ω) of vacancies and occupancies of N gas particles in M sites? Calculate the entropy. [1 point]

   (b) Using the relation between pressure and entropy, derive the ideal gas law. [2 points]

   (c) Show that to the next order of series expansion, the above definition of pressure leads to Van der Wall's equation:

   $$\left(P + \frac{aN^2}{V^2}\right)\left(\frac{V}{N} - b\right) = k_{_B}\,T$$

   where $a = 0$ and b is a constant. [2 points]

4. Consider an isolated (fixed total energy) system of N atoms each of which may exist in three states of energies $-\epsilon, 0, +\epsilon$. Let us specify the macrostates of the system by N, E (the total energy) and n, the number of atoms in the zero energy state.

   (a) Identify explicitly and write out the microstates corresponding to $N = 3, E = 0, n = 1$ and $N = 3, E = 0, n = 3$ macrostates (use $-, 0, +$ to denote the state of the atoms). [0.5 points]

   (b) If n_+ and n_- are the number of atoms in $+\epsilon$ and $-\epsilon$ states show that for a macrostate where $E = 0$ one has $n_+ = n_- = (N - n)/2$. [0.5 points]

   (c) Explain carefully why the weight of the macrostate $E = 0$, (and n is as above) is [1 point]

   $$^{N}C_{n}\;^{N-n}C_{(N-n)/2}$$

(d) Show that (for large N) the entropy of this macrostate is given by [1 point]

$$\frac{S(x)}{Nk_B} = -x\ln(x) - (1-x)\ln(1-x) + (1-x)\ln(2)$$

where $x = n/N$.

(e) What are the values of $S(0), S(1)$? Explain why. [0.5 points]

(f) Where is the maximum of $S(x)$? Explain why this is a maximum. [1 point]

(g) Sketch $S(x)$. [0.5 points]

Useful formulae

1. Stirling's approximation $\ln n! \simeq n\ln n - n$

2. Maxwell's relations are:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad dU = T\,dS - P\,dV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad dF = -S\,dT - P\,dV$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad dH = T\,dS + V\,dP$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad dG = -S\,dT + V\,dP$$

3.

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial y}{\partial x}\right)_z$$