

## Problem 1. Einstein Model of Solid

A solid consists of an array of atoms in a crystal structure shown below. In a simple model (used by Einstein at the advent of quantum mechanics) each atom is assumed to oscillate independently of every other atom<sup>1</sup>. The model has one free parameter  $\omega_0$  and predicts the general properties of specific heats of solids.

In one dimension a “solid” of  $N$  atoms consists of  $N$  independent harmonic oscillators. The Hamiltonian of each oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \quad (1)$$

where  $m$  is the mass of the atom. In two dimensions each atom can oscillate in the  $x$  direction and the  $y$  direction. Thus, the solid of  $N$  atoms consists of  $2N$  independent quantum oscillators. The Hamiltonian (or energy) of each atom is a sum of two harmonic oscillators:

$$H = H_x + H_y \quad (2)$$

$$= \left( \frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \right) + \left( \frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2 \right) \quad (3)$$

Finally in three dimensions (shown below) the solid of  $N$  atoms consists of  $3N$  independent oscillators as shown below, and each atom can oscillate in the  $x$ ,  $y$ , or  $z$  directions. The Hamiltonian of each atom shown in Fig. 1 consists of three harmonic oscillators:

$$H = H_x + H_y + H_z \quad (4)$$

$$= \left( \frac{p_x^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 \right) + \left( \frac{p_y^2}{2m} + \frac{1}{2}m\omega_0^2 y^2 \right) + \left( \frac{p_z^2}{2m} + \frac{1}{2}m\omega_0^2 z^2 \right) \quad (5)$$

The total Hamiltonian is a sum of the Hamiltonians of each atom.

- (a) By appealing to the equi-partition theorem for a classical harmonic oscillator, argue that the mean energy of the solid at temperature  $T$  is

$$E = 3NkT, \quad (6)$$

if the solid is treated as  $3N$  independent classical oscillators. Determine the specific heat  $C_V^{\text{lm}}$  for one mole of substance in this case.

- (b) When each the solid is treated as  $3N$  quantum harmonic oscillators, the energy of the solid is  $E = 3N \langle \epsilon \rangle$ , where the  $\langle \epsilon \rangle$  is the average energy of the a single harmonic oscillator. By reviewing the results of previous homework, write down the total energy of the solid at temperature  $T$ , and record the mean vibrational quantum number  $\bar{n}$  of a single oscillator.

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<sup>1</sup>In reality the motions of the atoms are coupled to each other, and the oscillation pattern of the solid, may be found by breaking it up into normal modes.

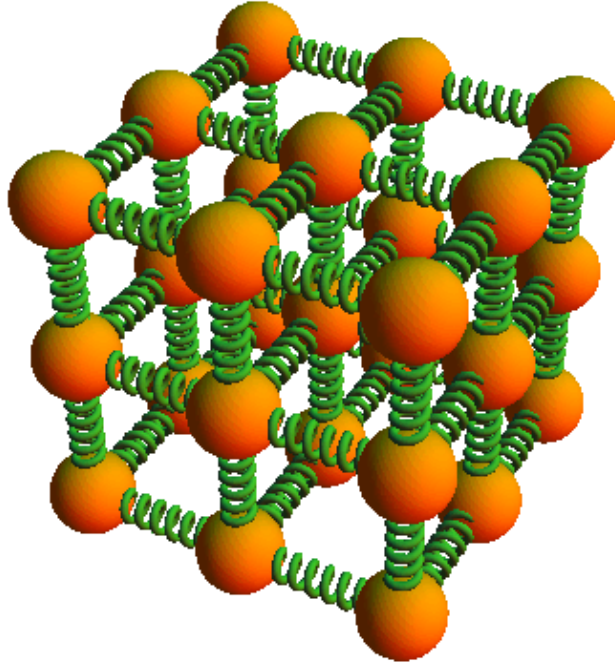


Figure 1:

- (c) The figure below shows  $N = 400$  harmonic oscillators in equilibrium sharing the total available energy. The numbers indicate the energy level  $n$  of each oscillator – if one oscillator gains a unit of energy, e.g. increasing from  $3\hbar\omega_0$  to  $4\hbar\omega_0$ , the rest of the oscillators will have one less unit of energy to share. Estimate the temperature of the system.

1	0	1	0	2	1	0	0	2	1	3	1	1	0	0	0	0	1	0
1	2	2	2	0	0	0	0	0	1	1	0	0	3	5	1	0	0	0
0	0	1	1	0	2	0	0	6	1	1	0	1	1	1	0	2	0	0
0	3	3	0	0	2	0	0	3	0	1	3	0	2	0	0	0	3	0
2	0	0	1	0	6	0	4	1	0	0	0	2	1	0	0	1	1	1
1	0	6	0	4	0	1	2	1	0	0	0	1	0	0	0	0	3	4
0	0	0	1	2	4	0	0	1	0	0	2	0	1	2	1	1	2	0
1	3	0	0	2	0	1	0	1	0	0	3	0	4	0	2	1	0	6
1	1	1	0	0	0	0	1	0	3	1	2	0	0	0	0	1	0	0
0	0	0	0	0	2	0	3	1	0	0	0	0	0	3	0	0	2	2
9	1	0	1	1	0	2	1	0	1	0	0	0	3	7	3	0	2	3
2	2	0	0	0	0	0	1	0	1	7	1	3	1	0	1	3	0	1
0	5	3	0	1	2	4	8	1	0	4	0	3	0	1	0	0	0	4
0	0	0	0	1	0	0	0	0	1	0	1	0	0	2	3	0	2	0
0	1	1	0	0	2	0	4	0	1	0	4	0	1	1	1	1	8	5
0	0	0	0	1	0	0	0	2	0	1	0	1	1	2	0	0	1	1
3	0	0	0	4	0	0	1	0	1	2	0	0	1	2	0	2	0	1
0	0	1	2	1	0	0	0	0	0	1	0	0	2	0	1	1	0	0
1	0	1	0	0	0	1	0	3	1	0	0	0	0	2	9	0	0	5
0	0	1	2	3	0	1	2	0	2	4	0	0	1	2	0	0	0	1

- (d) Show that the specific heat  $C_V$  for one mole of solid is<sup>2</sup>

$$C_V^{1\text{ml}} = 3R \frac{(\beta \hbar \omega_0)^2 \exp(-\beta \hbar \omega_0)}{(1 - \exp(-\beta \hbar \omega_0))^2}. \quad (8)$$

Make a Taylor series expansion of  $C_V^{1\text{ml}}$  at high temperature, including the just leading term. What is the specific heat in the ultimate high temperature limit? Your result should be consistent with part (a). Why?

- (e) I downloaded the specific heat of silver and made a graph of the Einstein prediction for  $C_V^{1\text{ml}}$ . The Einstein model has a free parameter  $\hbar \omega_0$ . The graph below shows the prediction for  $\hbar \omega_0 = 2E_0, E_0, E_0/2$  with  $E_0 = 0.013 \text{ eV}$ . The graph I get for silver is shown below (top) as well as the  $C_V$  for other substances (bottom).
- (i) Diamond is known to be a very hard substance. Loosely explain how this fact is reflected in the data on  $C_V$  presented in the figure below? *Hint*: What does the graph of  $C_V$  for different substances tell you about the relative strengths of the spring constants of the material?

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<sup>2</sup>When computing  $C_V$ , it may be helpful to recognize that

$$T \frac{\partial}{\partial T} = -\beta \frac{\partial}{\partial \beta} \quad (7)$$

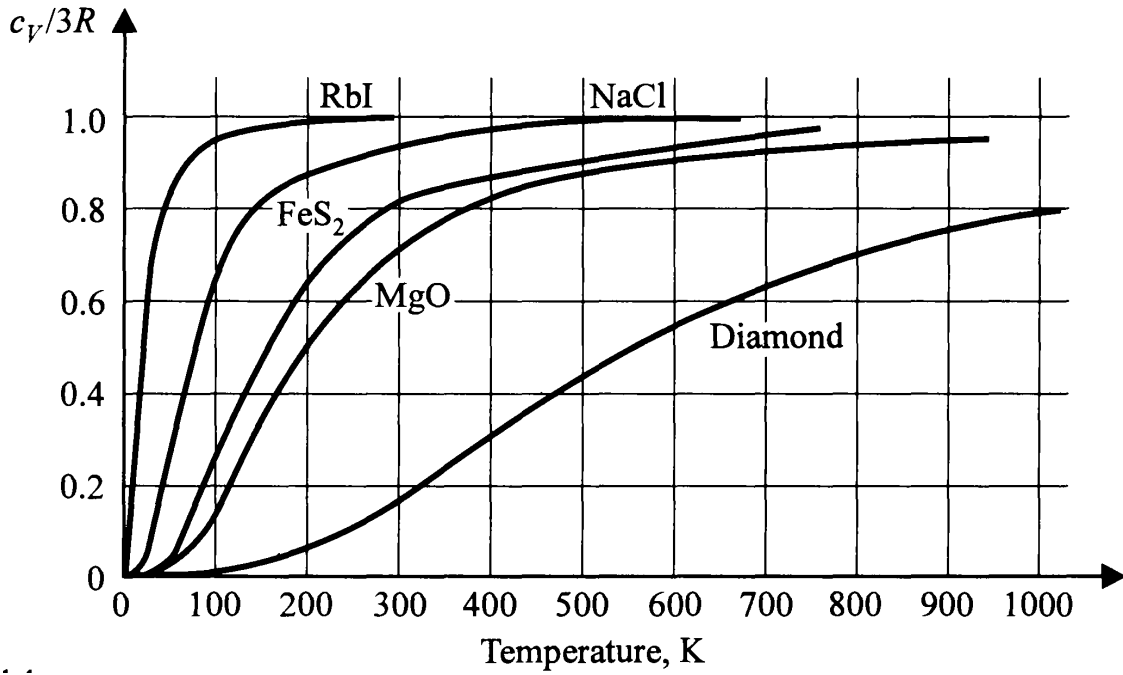
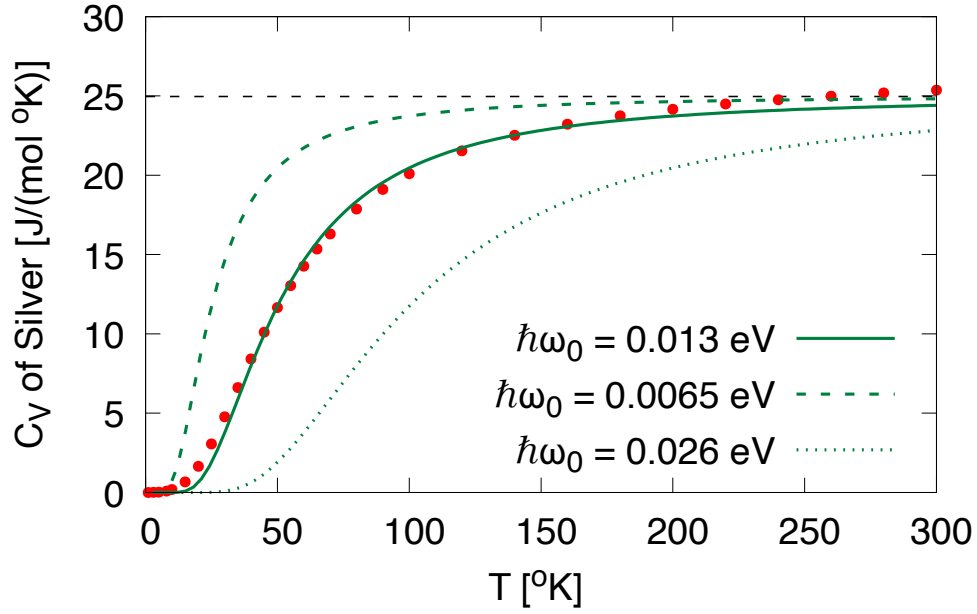


Figure 2: Specific heats of solids: (a) The Einstein Model with  $\hbar\omega_0$  treated as a parameter compared to the specific heat of silver. The graph approaches  $3R$  at high temperature. (b) The specific heat  $C_V$  in units of  $R$  of various solids versus temperature. The specific heat approaches  $3R$  at high temperature

## Problem 2. Entropy changes of a MAIG

Find the change in entropy of  $n_{\text{ml}}$  moles of an ideal monoatomic ideal gas in the following processes:

- (a) the temperature changes from  $T_1$  to  $T_2$  at constant pressure;
- (b) the pressure changes from  $P_1$  to  $P_2$  at constant volume.

Consider the expression for the number of states in a mono-atomic ideal gas

$$\Omega = C(N)V^N E^{3N/2}, \quad (9)$$

and the corresponding entropy

$$S = Nk_B \log(V) + \frac{3}{2}Nk_B \log(E) + \text{const}. \quad (10)$$

Recall that in an adiabatic expansion of a monoatomic ideal gas no heat enters or exits the system and the entropy remains constant as the volume increases.

- (c) (i) Using Eq. (10) show that  $\Delta S = 0$  for an adiabatic increase in volume from  $V_1$  to  $V_2$ . (*Hint:* How does the temperature change during an adiabatic expansion of a mono-atomic ideal gas?)
- (ii) Describe how the particles are redistributed in phase space so that the entropy and total phase space volume remains constant during the expansion.

Ans: (a)  $\frac{5}{2}n_{\text{ml}}R \ln(T_2/T_1)$ ; (b)  $\frac{3}{2}n_{\text{ml}}R \ln(P_2/P_1)$ .

### Problem 3. Entropy change in the mixing of hot and cold gasses

$N_1, T_1$	$N_2, T_2$
He	Ar

Consider two mono-atomic ideal gasses, Helium and Argon, separated by a divider which partitions a container of volume  $V$  into two equal parts. There are  $N_1$  Helium atoms on the left of the divider, and  $N_2$  Argon atoms on the right of the divider. The Helium atoms are initially at a temperature of  $T_1$ , while the Argon atoms are initially at a temperature of  $T_2$ . After the dividing wall is removed, the two gasses mix and ultimately equilibrate.

- (a) Determine the final temperature of the system  $T_f$ .
- (b) Determine the change in entropy of the system resulting from the mixing process in two ways:
  - (i) Directly count the number of states at the beginning and end.
  - (ii) For simplicity, first assume that  $T_1 = T_2$ . Identify an equilibrium path connecting the state at the beginning to the state at the end. Calculate the change in entropy during the process by analyzing the process using thermodynamics. Explain how the example illustrates the formula

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} > \frac{Q}{T} \quad (11)$$

- (iii) Now assume  $T_1 \neq T_2$ . Identify an equilibrium path (or sequence of paths) connecting the state at the beginning to the state at the end (the choice is not unique). Calculate the change in entropy during the process by analyzing the process using thermodynamics on this path<sup>3</sup>.

### Problem 4. Einstein Model from the Microcanonical Ensemble

Recall that temperature is a parameter which describes how the energy is shared, or partitioned, amongst its constituents.

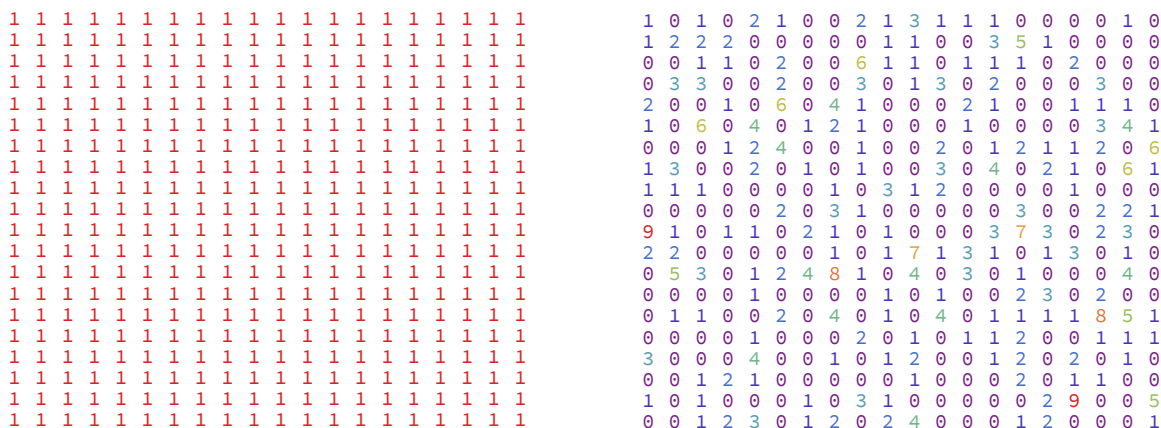
Recall that the entropy (divided by  $k_B$ ) is the logarithm of the number of ways a system can partition the total available energy into states or configurations.

Consider  $N$  quantum harmonic oscillators sharing total energy  $E$ . The total energy consists of  $q$  vibrational quanta of energy  $E \equiv q\hbar\omega_0$  ( $q$  is an integer). The figure below

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<sup>3</sup>*Hint:* Perhaps consider a path where the temperatures of the gasses first change  $T_f$  (at fixed volume) and then use path of part (b.ii).

## Ordered versus typical state:



Ordered state: one quantum of energy,  $\hbar\omega_0$ , per site

Typical state: on average one quantum per site, but the number in a given site can vary

Figure 3: Two equally likely configurations.

shows 400 harmonic oscillators sharing  $q = 400$  of energy. One possible configuration is that each atom has  $\hbar\omega_0$  of energy Fig. 3(a). Another configuration, which is more typical, is shown below in Fig. 3(b). Here some atoms have more energy and some have less. Each configuration is equally likely, and this problem will show that there are  $e^{555}$  of them.

- Show that for four atoms (quantum harmonic oscillators) and three quanta of energy ( $N = 4$  and  $q = 3$ ) show that there are 20 ways for the oscillators to share the energy. For instance, the first atom could have the three quanta and the rest none. That is one possible state.
- Each of the ways is to partition the total energy in part(a) is equally likely. What is the probability that one of the atoms will have all the energy? What is the probability that the *first* atom has two quanta? What is the probability that an atom will have two quanta<sup>4</sup>.
- Show that that there are

$$\Omega(q) = \frac{(N + q - 1)!}{q!(N - 1)!} \quad (12)$$

ways to distribute  $q$  units of energy amongst the  $N$  atoms.

*Hint:* Consider each oscillator to be a bin, and each bit of energy to be a ball. We are asking for the number of ways to put  $q$  balls in  $N$  bins.

Take seven balls (units of energy) and five bins (oscillators),  $N = 5$  and  $q = 7$ . Lay out the 7 energy units (balls) between the dashed lines.

<sup>4</sup>Answers: 4/20, 3/20, 12/20.



To partition the 7 energy units (balls) amongst the five oscillators (bins), I need four dividers, shown by the solid lines. In the figure below, I have paced the four dividers in one possible way, partitioning the energy so that the first bin has 2 units, the second bin has none, the third bin has 3, the fourth has two, and the fifth has none. The total number of objects (ball or divider) is  $q + (N - 1) = 11$ . Use this logic and the number of ways of choosing  $q$  of these objects to be balls to explain Eq. (12).

- (d) Show that for  $N = 400$  oscillators and  $q = 400$  quanta the number of states is approximately

$$e^{2N \ln 2} = e^{555} \quad (13)$$

- (e) Show more generally that for  $N$  oscillators and  $q$  quanta that

$$\Omega(E) = e^{N[(1+\bar{n}) \ln(1+\bar{n}) - \bar{n} \ln \bar{n}]} \quad (14)$$

where  $\bar{n} = q/N = E/(N\hbar\omega_0)$ . Show the entropy of the system is

$$S = Nk_B [(1 + \bar{n}) \log(1 + \bar{n}) - \bar{n} \log \bar{n}] \quad (15)$$

- (f) Starting from your results for  $S(E)$  show that

$$\frac{1}{T} = \frac{k_B}{\hbar\omega_0} \log \left( \frac{1 + \bar{n}}{\bar{n}} \right) \quad (16)$$

- (g) Rearrange Eq. (16) to show that  $\bar{n}$  is related to the temperature as before:

$$\bar{n} = \frac{1}{e^{\beta\hbar\omega_0} - 1}. \quad (17)$$

Do not *use* the results of the previous problem in any way – just compare the result.

- (h) Take Fig 3(b) shown above. A histogram is made of the the number of atoms  $N(n)$  with  $n$  units of energy, with  $n$  an integer (see Fig. 4 for an example). Give a function of  $n$  which would approximately describe the histogram.

(answer:  $N(n) \simeq 200 \exp(-0.7n)$ )

**Discussion:** We have computed properties of the solid in two ways. The first method, uses the partition functions at a fixed temperature. It works with an independent subsystem which have probability

$$P_m^{\text{sub}} = \frac{1}{Z} e^{-\beta\epsilon_m}. \quad (18)$$

to be in microstate  $m$  of the subsystem. This probability distribution is known as the canonical ensemble. It is technically easier.



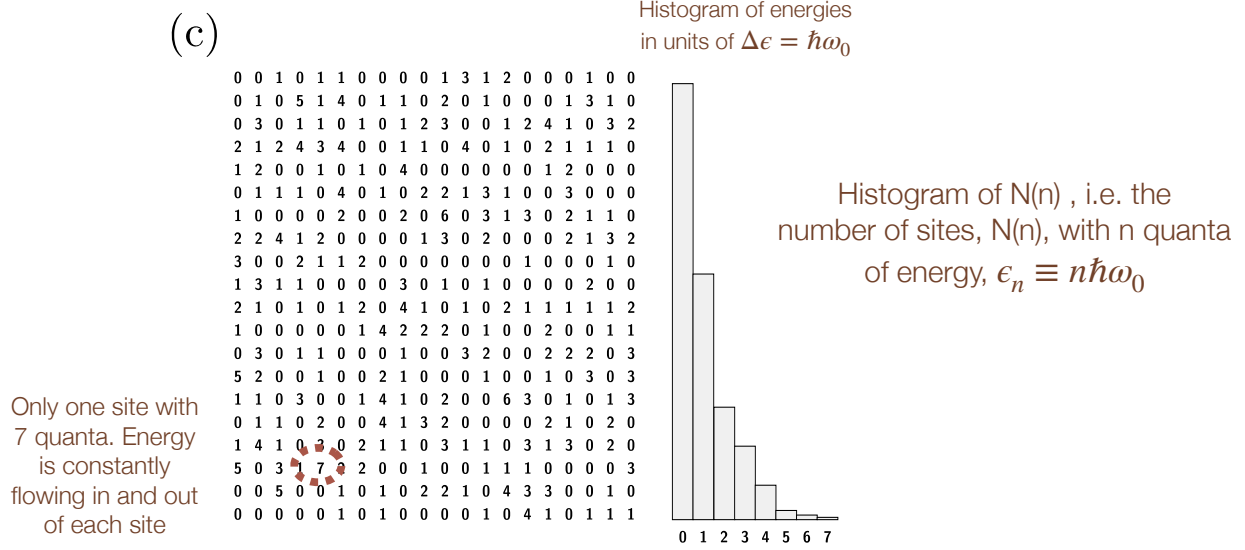


Figure 4: Histogram of energies

The second method, directly counts the number of states of the total system to find the total entropy at a fixed total energy. The probability to be in a microstate of the full system is

$$P_m^{\text{full}} = \text{const.} = \frac{1}{\Omega(E)} \quad (19)$$

This probability distribution is known as the micro-canonical ensemble. It is conceptually important. The two ensembles are equivalent. They should be. We derived the Boltzmann factor and the canonical distribution from the entropy of the microcanonical ensemble.

## Problem 5. Simple Steps

Each of these consists of small algebra and definitions.

- (a) The probability of a system being in the  $i$ th microstate is

$$P_i = e^{-\beta E_i} / Z, \quad (20)$$

where  $E_i$  is the energy of the  $i$ th microstate and  $\beta$  and  $Z$  are constants. From the Gibbs expression for the entropy  $S = -k_B \sum_m P_m \ln P_m$  show that the entropy is related to  $Z$

$$\frac{S}{k_B} = \ln Z + \beta U \quad (21)$$

where  $U = \sum P_i E_i$ . Also show that

$$Z = e^{-\beta F} \quad F = -kT \log Z \quad (22)$$

- (b) Starting from the first Law  $dE = TdS - pdV$  (i) derive the expression for  $dF$  in terms of its natural variables  $(T, V)$  and (ii) derive an expression for  $dG$  in terms of its natural variables  $(T, P)$  (iii) Derive the Maxwell relation stemming from  $dF$  and  $dG$ .

(c) Show the following

$$U = - T^2 \left( \frac{\partial(F/T)}{\partial T} \right)_V \quad (23)$$

$$C_V = - T \left( \frac{\partial^2 F}{\partial T^2} \right)_V \quad (24)$$

$$H = - T^2 \left( \frac{\partial(G/T)}{\partial T} \right)_p \quad \text{Optional} \quad (25)$$

$$C_p = - T \left( \frac{\partial^2 G}{\partial T^2} \right)_p \quad \text{Optional} \quad (26)$$