

## 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.

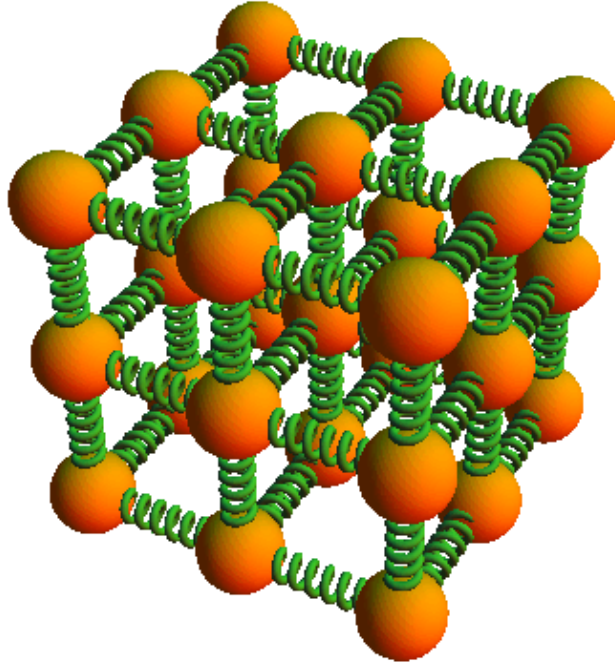


Figure 1:

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

- (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

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

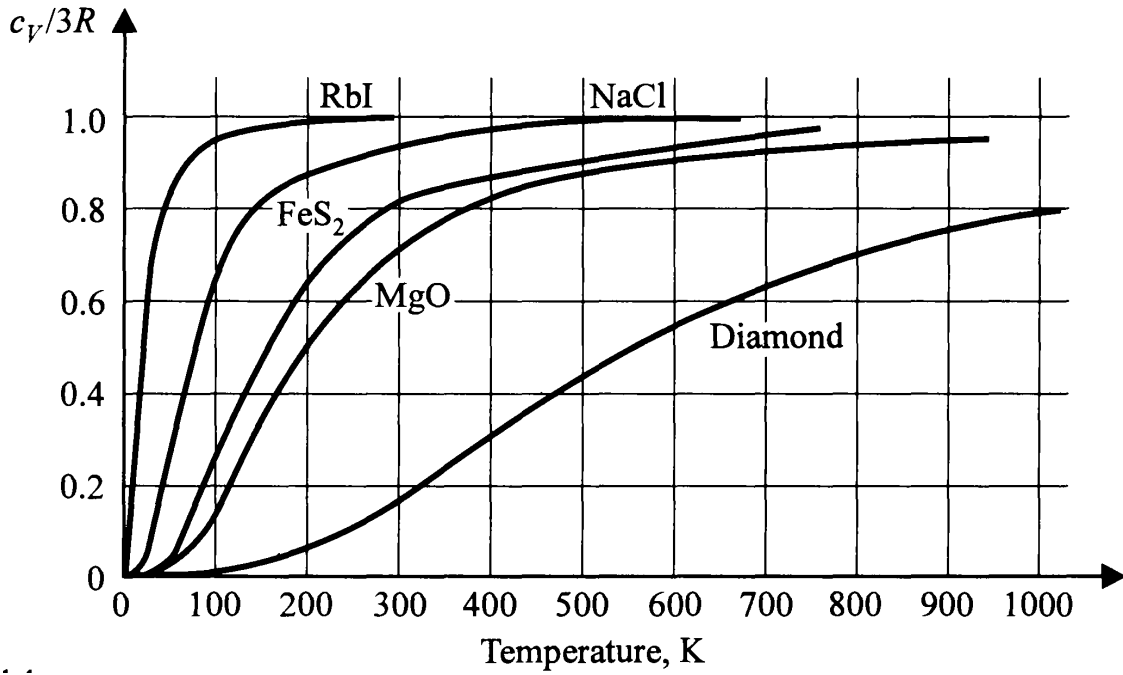
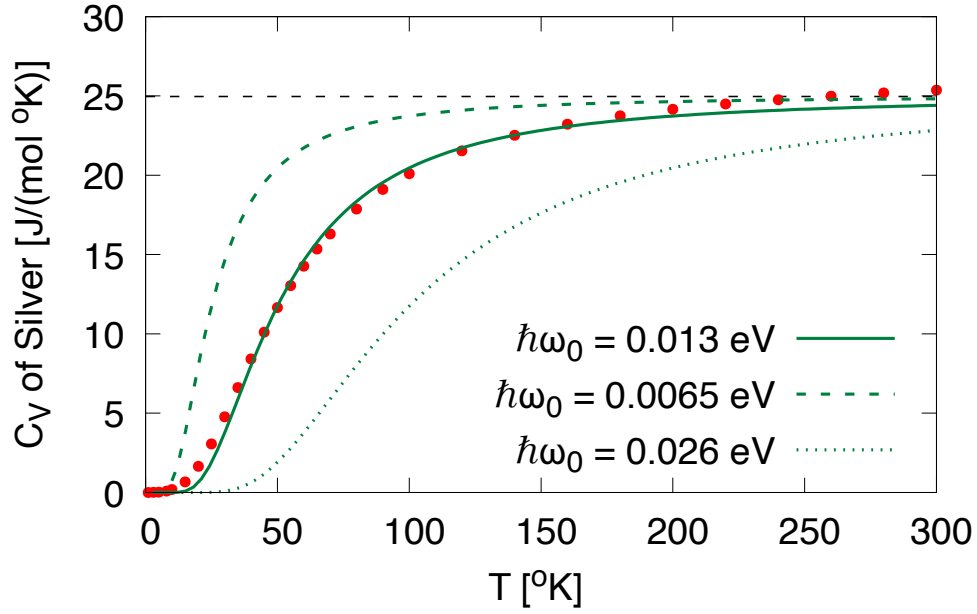


Figure 2: Specific heats of solids: (a) The Einstein Model with  $\hbar\omega_0$  treated as a parameter compared to the specific heat of silver. The graph approaches  $3R$  at high temperature. (b) The specific heat  $C_V$  in units of  $R$  of various solids versus temperature. The specific heat approaches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

## Einstein Solid

- a) There are  $3N$  oscillators. The Hamiltonian of the oscillator is

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

two quadratic forms

$$\text{So, } \bar{E} = 3N \times 2 \times \frac{1}{2} kT \approx 3NkT$$

Now  $C_V = \partial E / \partial T$ .

So for  $N = 1 \text{ mol}$

$N_A k_B = R$ , and so

$$C_V^{\text{lm}} = 3R$$

b)  $E = 3N \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}$        $\bar{n} = \frac{1}{e^{\beta \hbar \omega} - 1}$

- c) Solving for  $\beta$  from  $\bar{n}$  (to make contact with later work in the next problem)

$$\frac{1}{\bar{n}} = e^{\beta \hbar \omega} - 1 \Rightarrow e^{\beta \hbar \omega} = 1 + \frac{1}{\bar{n}}$$

So

$$\beta \hbar \omega = \ln \left( \frac{1 + \bar{n}}{\bar{n}} \right) \Rightarrow \frac{1}{kT} = \frac{1}{\hbar \omega} \ln \left( \frac{1 + \bar{n}}{\bar{n}} \right)$$

Now we can estimate the  $\bar{n}$  by counting up the numbers in the figure and dividing by 400 (the number of atoms). Doing this we find  $\bar{n} = 1$ . So  $\beta \hbar \omega = \ln((1+1)/1) = \ln(2)$  and  $kT = \hbar \omega / \ln(2)$ .

d) We know that

$$C_v = \left( \frac{\partial E}{\partial T} \right) \quad \text{with} \quad E = 3N \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}$$

We use that for any quantity  $X$

$$\frac{\partial X}{\partial T} = \frac{\partial X}{\partial \beta} \frac{\partial \beta}{\partial T} = \frac{\partial X}{\partial \beta} \frac{\partial}{\partial T} \left( \frac{1}{kT} \right)$$

$$\boxed{\frac{\partial X}{\partial T} = -k\beta^2 \frac{\partial X}{\partial \beta}}$$

So

$$C_v = -k\beta^2 \frac{\partial}{\partial \beta} \left( \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right)$$

Differentiating

$$C_v = 3Nk\beta^2 \frac{(\hbar \omega)^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

For 1 mol  $N = N_A$   $N_A k_B = R$

$$\boxed{C_v^{1\text{mol}} = 3R \frac{(\beta \hbar \omega)^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}}$$

In the high temperature limit the mean # of quanta in the oscillator gets larger and larger. In this limit the dynamics should be classical, (see previous homework)

Expanding for  $\beta\hbar\omega \ll 1$  (high temperature), we approximate:

$$e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$$

And

$$C_v^{lm} \approx 3R \frac{(\beta\hbar\omega)^2}{(1 + \beta\hbar\omega - 1)^2} (1)$$

$$C_v^{lm} \approx 3R$$

↑ this agrees with part (a)  
as it should

(e) The hard materials have a larger  $\omega_0 = \sqrt{k/m}$ . They have, therefore, a larger spring constant,  $k$ . Because  $\omega_0$  is higher for diamond  $C_v$  will approach the classical limit  $3R$  only at very high temperatures  $kT \gg \hbar\omega_0$ , when the number of vibrational quanta is large.

## 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)  $\frac{3}{2}n_{\text{ml}}R \ln(P_2/P_1)$ .



## Entropy Changes of Ideal Gas

↙ This is the entropy of a MAIG, which we derived. We will use this in this problem

$$(★) S = Nk \ln V + \frac{3Nk}{2} \ln E + \text{const}$$

$$a) PV = NkT, \text{ so for } P \text{ const, } \frac{V_1}{V_2} = \frac{T_1}{T_2} = \frac{E_1}{E_2}$$

$$\text{Since } E = \frac{3}{2} NkT \propto T,$$

$S_0$

$$\Delta S = S_2 - S_1$$

$$= Nk \ln \frac{V_2}{V_1} + \frac{3Nk}{2} \ln \frac{E_2}{E_1}$$

$$= Nk \ln \frac{T_2}{T_1} + \frac{3}{2} Nk \ln \frac{T_2}{T_1}$$

$$\Delta S = \frac{5Nk}{2} \ln \frac{T_2}{T_1}$$

$$b) \Delta S = S_2 - S_1$$

$$= Nk \ln \frac{V_2}{V_1} + \frac{3Nk}{2} \ln \frac{E_2}{E_1} \quad \text{now } PV = NkT$$

$$P \propto T \propto E$$

↙ constant volume

So

$$\Delta S = \frac{3}{2} Nk \ln \left( \frac{P_2}{P_1} \right)$$

c) Now for an adiabatic expansion

$$TV^{\gamma-1} = \text{const}$$

this is for a  
MAIG

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} \quad \text{where } \gamma = \frac{5}{3}$$

or

$$\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{2/3}$$

$$\frac{E_2}{E_1} = \frac{T_2}{T_1} = \left( \frac{V_2}{V_1} \right)^{-2/3}$$

So

$$\Delta S = Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \frac{T_2}{T_1}$$

$$(i) \quad = Nk \ln \frac{V_2}{V_1} + \frac{3}{2} Nk \ln \left( \frac{V_2}{V_1} \right)^{-2/3} = 0$$

(ii) The coordinate space volume is getting bigger, but the momentum space volume is getting smaller as the temperature drops. We have  $EV^{3/2} = \text{const}$  during the adiab expansion of a MAIG.

### 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>.

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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).

## Entropy change in the mixing of Hot & Cold Gasses

(a) Energy is conserved and the gasses ultimately have the same temperature.

$$E_1 + E_2 = E$$

$$\frac{3}{2} N_1 k T_1 + \frac{3}{2} N_2 k T_2 = \frac{3}{2} (N_1 + N_2) k T$$

$$\frac{N_1 T_1 + N_2 T_2}{(N_1 + N_2)} = T$$

(b) The entropy of Each Gas is

$$S = Nk \ln V + \frac{3}{2} Nk \ln E + \text{const}$$

$$E \propto T$$

$$S = Nk \ln V + \frac{3}{2} Nk \ln T + \text{const}$$

← a different constant

So

$$\Delta S = Nk \ln \frac{V_f}{V_i} + \frac{3}{2} Nk \ln \frac{T_f}{T_i}$$

Here we have two gasses:

$$\frac{V_f}{V_i} = \frac{V}{V/2} = 2$$

$$\frac{T_f}{T_i} = \frac{T}{T_1} \quad \text{for gas \#1}$$

$$\frac{T_f}{T_i} = \frac{T}{T_2} \quad \text{for gas \#2}$$

$S_0$

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$\Delta S = (N_1 + N_2) k \ln 2 + \frac{3}{2} N_1 k \ln \frac{T}{T_1} + \frac{3}{2} N_2 k \ln \frac{T}{T_2}$$

The thermodynamic argument for the change in entropy (just found) goes as follows. Take gas 1. It's initial state and final states are

$$(T_1, V_1 = \frac{V}{2}) \rightarrow (T_f, V) \quad (12)$$

Since entropy only depends on the state, and not on how you got there, we can pick any convenient equilibrium path to get from the initial state to the final state. The actual system did not follow this path. Then we can evaluate the entropy change using

$$dS = \frac{dQ_{\text{rev}}}{T}. \quad (13)$$

This formula assumes the system is in equilibrium with a reservoir at temperature  $T$ , which was not the case here. Here no heat flowed from the environment to the system. The initial and final states of gas 2 are

$$(T_2, V_2 = \frac{V}{2}) \rightarrow (T_f, V) \quad (14)$$

A convenient choice of path is: (*Step 1*) first leave the volume constant and increase the temperature; (*Step 2*) then leave the temperature fixed and increase the volume.

*Step 1*: In the first step the work done is zero since volume is constant. So  $dQ_{\text{rev}} = C_V dT$  where  $C_V = (3/2)N_1k$  is the specific heat of a MAIG. Thus for gas number 1 in step 1 we have:

$$\Delta S_{1,1} = \int C_V \frac{dT}{T} = C_V \ln(T_f/T_i) = \frac{3}{2}N_1k \ln(T_f/T_1) \quad (15)$$

Similarly for gas number 2 in step 1 one we have:

$$\Delta S_{2,1} = \frac{3}{2}N_2k \ln(T_f/T_2) \quad (16)$$

*Step 2*: Then in the second step the temperature is constant, but the volume increases. The energy is also constant, since for an ideal gas the energy is only a function of temperature, which is constant. So, in the second step  $dU = 0$  and  $dQ_{\text{rev}} = p_1 dV$  by the first law ( $dU = dQ - p dV$ ). Thus we find

$$\Delta S_{1,2} = \int \frac{dQ_{\text{rev}}}{T} = \int_{V_1}^V \frac{p_1}{T} dV = N_1k \ln(2) \quad (17)$$

Similarly, for gas number 2 in step 2

$$\Delta S_{2,2} = N_2k \ln(2) \quad (18)$$

Putting together the contributions, we find:

$$\Delta S = \Delta S_{1,1} + \Delta S_{2,1} + \Delta S_{1,2} + \Delta S_{2,2} \quad (19)$$

$$= (N_1 + N_2)k \ln(2) + \frac{3}{2}N_1k \ln(T_f/T_1) + \frac{3}{2}N_2k \ln(T_f/T_2) \quad (20)$$

which agrees with the previous method.

**Discussion:** In each step, we assumed that gas 1 and gas 2 were in equilibrated contact with a reservoir at temperature  $T$ . This approach is valid (although not reality) because we are using these fictitious reservoir to find the change in entropy of the system, which only depends on the initial and final states, which are in complete equilibrium. But, it must be understood that in reality no heat is exchanged with the environment and  $dQ = 0$ . In general the change in entropy of the system (which can be computed by assuming a reversible exchange of heat with a reservoir) is larger than the actual heat that flows into the system from a reservoir at temperature  $T$ :

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} > \frac{Q}{T} \quad (21)$$

In this specific problem  $Q = 0$  and we found

$$\Delta S = \int \frac{dQ_{\text{rev}}}{T} = (N_1 + N_2)k \ln(2) + \frac{3}{2}N_1k \ln(T_f/T_1) + \frac{3}{2}N_2k \ln(T_f/T_2) > 0 \quad (22)$$

Clearly  $\Delta S > 0$  and the process is irreversible.

## Problem 4. Simple Steps

Each of these consists of small algebra and definitions.

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

$$P_i = e^{-\beta E_i} / Z, \quad (23)$$

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  $Z$

$$\frac{S}{k_B} = \ln Z + \beta U \quad (24)$$

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

$$Z = e^{-\beta F} \quad F = -kT \log Z \quad (25)$$

- (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

$$U = - T^2 \left( \frac{\partial(F/T)}{\partial T} \right)_V \quad (26)$$

$$C_V = - T \left( \frac{\partial^2 F}{\partial T^2} \right)_V \quad (27)$$

$$H = - T^2 \left( \frac{\partial(G/T)}{\partial T} \right)_p \quad \text{Optional} \quad (28)$$

$$C_p = - T \left( \frac{\partial^2 G}{\partial T^2} \right)_p \quad \text{Optional} \quad (29)$$



### Simple Steps

$$a) \quad P_i = \frac{e^{-\beta E_i}}{Z}$$

$$\begin{aligned} \frac{S}{k_B} &= - \sum_i P_i \ln P_i \\ &= - \sum_i \frac{e^{-\beta E_i}}{Z} \ln \frac{e^{-\beta E_i}}{Z} \end{aligned}$$

$$= - \sum_i \frac{e^{-\beta E_i}}{Z} (-\beta E_i) + \sum_i \frac{e^{-\beta E_i}}{Z} \ln Z$$

$$= \sum_i \frac{e^{-\beta E_i}}{Z} (-\beta E_i) + \ln Z \sum_i \frac{e^{-\beta E_i}}{Z}$$

$$\boxed{\frac{S}{k_B} = \beta \bar{E} + \ln Z}$$

$$\text{So } \ln Z = \frac{S}{k_B} - \frac{\bar{E}}{k_B T} = -\frac{F}{k_B T}$$

And

$$\boxed{Z = e^{-F/k_B T}}$$

$$b) \quad du = Tds - pdv$$

$$d(u - TS) = Tds - pdv - (Tds + SdT)$$

$$F \equiv u - TS \quad dF = -SdT - pdv$$

$$d(F + pV) = -SdT - pdv + (pdv + Vdp)$$

$$G = u - TS + pV \quad \boxed{dG = -SdT + Vdp}$$

$$c) \quad S_0$$

$$-T^2 \left( \frac{\partial (F/T)}{\partial T} \right)_V = F - \left( T \frac{\partial F}{\partial T} \right)_V = F + TS$$

we used  $dF = -SdT - pdv$ . Then since  $F = u - TS$ , we have

$$i) \quad -T^2 \frac{\partial (F/T)}{\partial T} = u \quad \checkmark$$

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

iii)

$$-T^2 \left( \frac{\partial (G/T)}{\partial T} \right)_P = G - T \left( \frac{\partial G}{\partial T} \right)_P = G - T(-S) = G + TS$$



But  $G = U - TS + pV$  and  $H = U + pV$  and so

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

So

$$C_p = T \left( \frac{\partial S}{\partial T} \right)_p = T \left( \frac{\partial}{\partial T} \right)_p \cdot \left( \frac{\partial G}{\partial T} \right)_p = T \left( \frac{\partial^2 G}{\partial T^2} \right)_p \quad \checkmark$$