

# Physics 406 Homework

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## 1 Homework 1

### Problem 1.1

Prove that the quantity  $S = -k \sum_{r=1}^n p_r \ln(p_r)$  is a maximum when  $p_r = \frac{1}{n}$ . You may need to use the inequality:

$$\ln\left(\frac{1}{np_r}\right) \leq \left(\frac{1}{np_r} - 1\right)$$

This completes the proof that the choice of equal relative probabilities for the states in a microcanonical ensemble maximizes missing information (entropy).

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**Problem 1.2** *Reif 2.3*

Consider an ensemble of classical 1-D Harmonic oscillators.

- (a) Let the displacement  $x$  of an oscillator as a function of time  $t$  be given by  $x = A \cos(\omega t + \varphi)$ . Assume that the phase angle  $\varphi$  is equally likely to assume any value  $0 < \varphi < 2\pi$ . The probability  $w(\varphi)d\varphi$  that  $\varphi$  lies in the range between  $\varphi, \varphi + d\varphi$  is then simply

$$w(\varphi)d\varphi = \frac{d\varphi}{2\pi}$$

For any fixed time  $t$ , find the probability  $P(x)dx$  that  $x$  lies between  $x + dx$  by summing  $w(\varphi)d\varphi$  over all angles for which  $x$  lies in this range. Express  $P(x)$  in terms of  $A, x$ .

- (b) Consider the classical phase space for such an ensemble of oscillators, their energy being known to lie in the small range between  $E, E + \delta E$ . Calculate  $P(x)$  by taking the ratio of that volume of phase space lying in this energy range *and* in the range between  $x, x + dx$  to the total volume of phase space lying in the energy range between  $E, E + \delta E$ . Express  $P(x)$  in terms of  $E, x$ . By relating  $E$  to the amplitude  $A$ , show that the result is the same as that obtained in (a)
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**Problem 1.3**

Consider an assembly of  $N$  weakly interacting one dimensional harmonic oscillators, each with a mass  $m$  and frequency  $\omega$ .

- (a) Describe the region of phase space that is accessible to this system if its energy lies between  $E$  and  $E + \delta E$ .
- (b) Use phase space considerations to find how entropy of this system depends on  $E$ . (There will be an additive constant independent of  $E$  which you need not determine.)
- (c) How would a microstate of this system be described in quantum mechanical terms?

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What does weakly interacting mean? How do we define it, interacting with the system? not each other?

**Problem 1.4**

Suppose that a particle moving in one dimension is confined to  $x > 0$ , and its energy is  $E = \frac{p^2}{2m} + mgx$ . Make a sketch to indicate what region of classical phase space is accessible to this particle if its energy lies between  $E_0$  and  $E_0 + \delta E_0$ .

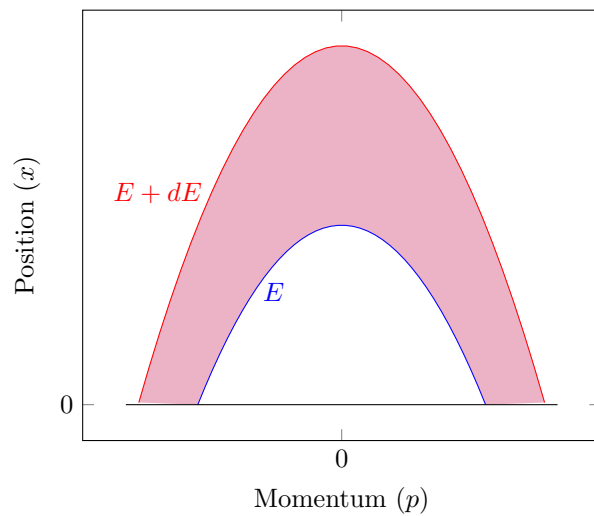


Figure 1: Particle constrained between blue and red curves.

## 2 Homework 2

### Problem 2.1

- (a) Show that the number of states  $\phi(E)$  with energy less than  $E$ , for a particle of mass  $m$  in a cubical box of side  $L$  is:

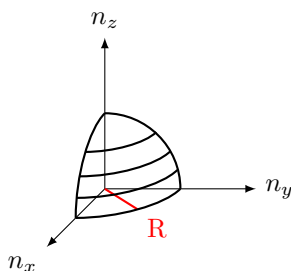
$$\phi(E) = \frac{\pi}{6} \left( \frac{L}{\pi \hbar} \right)^3 (2mE)^{3/2}$$

Hint: Use the energy levels 2.1.3 in Reif and treat the  $n$  as continuous variables.

$$\text{Reif 2.1.3: } E = \frac{(\hbar\pi)^2}{2m} \left[ \left( \frac{n_x}{L_x} \right)^2 + \left( \frac{n_y}{L_y} \right)^2 + \left( \frac{n_z}{L_z} \right)^2 \right]$$

- (b) Calculate  $\Omega(E)$
- (c) A nitrogen molecule at room temperature has a typical energy of  $6 \times 10^{-14}$  ergs. Calculate  $\phi(E)$  for a particle in a box of side length 10cm. Also calculate  $\Omega(E)$  assuming  $\delta E = 10^{-24}$  ergs

- a) Reif 2.1.3 can be simplified, knowing that the box is a cube implies that  $L_x = L_y = L_z \equiv L$ . The remaining  $n_x, n_y, n_z$  describe a sphere of radius  $R = \sqrt{n_x^2 + n_y^2 + n_z^2}$  in phase space.



$$E = \frac{(\hbar\pi)^2}{2mL^2} [n_x^2 + n_y^2 + n_z^2]$$

All possible states for the system are contained in this sphere. Since we can assume  $n_x, n_y, n_z$  are continuous,  $\phi(E)$  is just the volume of this slice of the sphere ( $V = \frac{1}{8} \frac{4}{3} \pi R^3$ ):

$$\boxed{\phi(E) = \frac{1}{8} \frac{4}{3} \pi R^3} \rightarrow \boxed{\phi(E) = \frac{\pi}{6} \left( \sqrt{2mE} \frac{L}{\hbar\pi} \right)^3} \rightarrow \boxed{\phi(E) = \frac{\pi}{6} \left( \frac{L}{\pi\hbar} \right)^3 (2mE)^{3/2}} \quad \checkmark$$

$$\text{b) } \Omega(E) = \phi(E + \delta E) - \phi(E) = \frac{\phi(E + \delta E) - \phi(E)}{\delta E} \delta E = \frac{d\phi}{dE} \delta E$$

$$\Omega(E) = \frac{d\phi}{dE} \delta E = \frac{\pi}{6} \left( \frac{L}{\pi\hbar} \right)^3 \left( \frac{3}{2} \right) (2m)^{1/2} (2mE)^{1/2} \delta E$$

$$\Omega(E) = \frac{m\pi}{2} \sqrt{2mE} \left( \frac{L}{\pi\hbar} \right)^3 \delta E$$

- c) Find energy in joules, plug in to phi equation with other units, or just use cgs

**Problem 2.2** *Reif 2.4*

Consider an isolated system consisting of a large number  $N$  of weakly interacting localized particles of spin  $\frac{1}{2}$ . Each particle has a magnetic moment  $\mu$  which can point either parallel or antiparallel to an applied field  $H$ . The energy of the system is then  $E = -(n_1 - n_2)\mu H$ , where  $n_1$  is the number of spins aligned parallel to  $H$  and  $n_2$  is the number of spins aligned antiparallel to  $H$ .

- (a) Consider the energy range between  $E + \delta E$  where  $\delta E$  is much smaller than  $E$ , but  $E$  is still microscopically large, so  $\mu H \ll \delta E \ll E$ . What is  $\Omega(E)$  (the total number of states in the energy range)?
- (b) Write down an expression for  $\ln(\Omega(E))$  as a function of  $E$ . Simplify this expression by using Stirling's formula in its simplest form:

$$\ln(n!) \approx n \ln(n) - n$$

- (c) Assume that the energy  $E$  is in a region where  $\Omega(E)$  is appreciable  $\rightarrow$  that it is not close to the extreme possible values  $\pm N\mu H$  which it can assume. In this case apply a Gaussian approximation to part (a) to obtain a simple expression for  $\Omega(E)$  as a function of  $E$ .

- a) Using the equation  $E = -(n_1 - n_2)\mu H$  and knowing that

$$\Omega(E) = {}_N C_{n_1} \delta E = \frac{N!}{n_1!(N - n_1)!} = \frac{N!}{n_1!n_2!} \delta E$$

$$E = -(n_1 - n_2)\mu H = -(n_1 - (N - n_1))\mu H = -(2n_1 - N)\mu H$$

$$\boxed{n_1 = \frac{N}{2} - \frac{E}{2\mu H} \quad , \quad n_2 = \frac{N}{2} + \frac{E}{2\mu H}}$$

$$\delta E = | - 2\delta n \mu H |$$

$$\Omega(E) = \frac{N!}{\left(\frac{N}{2} - \frac{E}{2\mu H}\right)! \left(\frac{N}{2} + \frac{E}{2\mu H}\right)!} \frac{\delta E}{2\mu H}$$

- b)  $\ln \Omega(E) = \ln(N!) - \ln(n_1!) - \ln(n_2!) + \ln(2\mu H \delta n)$

Now, using Stirling's approximation:

$$\ln \Omega(E) \approx N \ln(N) - N - (n_1 \ln(n_1) - n_1) - (n_2 \ln(n_2) - n_2) + \ln(2\mu H \delta n)$$

$$\approx N \ln(N) - \cancel{N} - n_1 \ln(n_1) + \left(\frac{\cancel{N}}{2} - \frac{\cancel{E}}{2\mu H}\right) - n_2 \ln(n_2) + \left(\frac{\cancel{N}}{2} + \frac{\cancel{E}}{2\mu H}\right) + \ln(2\mu H \delta n)$$

$$\ln \Omega(E) \approx N \ln(N) - n_1 \ln(n_1) - n_2 \ln(n_2) + \ln(2\mu H \delta n)$$

$$\ln \Omega(E) \approx N \ln(N) - \left(\frac{N}{2} - \frac{E}{2\mu H}\right) \ln\left(\frac{N}{2} - \frac{E}{2\mu H}\right) - \left(\frac{N}{2} + \frac{E}{2\mu H}\right) \ln\left(\frac{N}{2} + \frac{E}{2\mu H}\right) + \ln\left(\frac{\delta E}{2\mu H}\right)$$



**Problem 2.3** *Reif 2.5*

Consider the infinitesimal quantity

$$A(x, y)dx + B(x, y)dy \equiv dF$$

- (a) Suppose  $dF$  is an exact differential so that  $F = F(x, y)$ . Show that  $A, B$  must satisfy the condition:

$$\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}$$

- (b) If  $dF$  is an exact differential, show that the integral  $\int dF$  evaluated along any closed path on the  $xy$  plane must vanish.

- a) Using the definition of  $F$  with exact differentials:

$$Adx + Bdy = dF = \frac{\partial F}{\partial x}dx + \frac{\partial F}{\partial y}dy$$

$$Adx = \frac{\partial F}{\partial x}dx \quad , \quad Bdy = \frac{\partial F}{\partial y}dy \rightarrow \frac{\partial A}{\partial y} = \frac{\partial F}{\partial xy} = \frac{\partial B}{\partial x} \quad \checkmark$$

- b)  $dF$  is exact  $\iff \int_a^b dF = F(b) - F(a)$ .

Closed path  $\implies a=b$ .

$$\int_a^a dF = F(a) - F(a) = 0 \quad \checkmark$$

**Problem 2.4** *Reif 2.7*

- (a) Consider a particle confined to a cubical box. The possible energy levels are given by

$$E = \frac{(\hbar\pi)^2}{2m} \left[ \left( \frac{n_x}{L_x} \right)^2 + \left( \frac{n_y}{L_y} \right)^2 + \left( \frac{n_z}{L_z} \right)^2 \right]$$

Show that the force exerted by the particle in this state on a wall perpendicular to the  $x$  axis is given by

$$F_x = -\frac{\partial E}{\partial L_x}$$

while the length  $L_x$  is changed quasi-statically by an amount  $dL_x$ .

- (b) Calculate explicitly the pressure on this wall. By averaging over all possible states, find an expression for the mean pressure on this wall (Hint: Exploit the property that  $\overline{n_x^2} = \overline{n_y^2} = \overline{n_z^2}$  must be true by symmetry.) Show that the mean pressure can be simply expressed in terms of mean energy  $\overline{E}$  of the particle and the volume  $V = L_x L_y L_z$  of the box.

- a) As  $[L_x \rightarrow L_x + dL_x]$ ,  $[E \rightarrow E + dE]$ . This means that  $dE = [?]dL_x$  for some constant. **Since this is a quasi-static process? What about adiabatic? Is there heat?**

$$\frac{\partial E}{\partial L_x} = \frac{(-2)(\hbar\pi n_x)^2}{2mL_x^3} = \frac{-(\hbar\pi n_x)^2}{mL_x^3}$$

$$F_x = -\frac{\partial E}{\partial L_x} = \frac{(\hbar\pi n_x)^2}{mL_x^3}$$

- b) Pressure  $P_x$  is equivalent to force over area, so  $P_x = F_x/A_x$ . The area  $A_x$  of the wall perpendicular to the  $x$  axis is just  $L_y L_z$ . Since the box is cubical,  $L_x = L_y = L_z$  and  $\overline{n_x^2} = \overline{n_y^2} = \overline{n_z^2}$ .

$$\overline{E} = \frac{(\hbar\pi)^2}{2m} \left( \left( \frac{\overline{n_x}}{L_x} \right)^2 + \left( \frac{\overline{n_y}}{L_y} \right)^2 + \left( \frac{\overline{n_z}}{L_z} \right)^2 \right) = \frac{(\hbar\pi)^2}{2m} 3 \left( \frac{\overline{n_x}}{L_x} \right)^2$$

$$P_x = \frac{F_x}{L_y L_z} = \frac{(\hbar\pi n_x)^2}{mL_x^3 L_y L_z} = \frac{(\hbar\pi)^2}{mL_x L_y L_z} \left( \frac{n_x}{L_x} \right)^2 = \frac{(\hbar\pi)^2}{mV} \left( \frac{n_x}{L_x} \right)^2$$

$$\overline{P}_x = \frac{(\hbar\pi)^2}{mV} \left[ \left( \frac{\overline{n_x}}{L_x} \right)^2 \right] \rightarrow \left( \frac{\overline{n_x}}{L_x} \right)^2 = \frac{2m\overline{E}}{3(\hbar\pi)^2}$$

$$\overline{P}_x = \frac{(\hbar\pi)^2}{mV} \frac{2m\overline{E}}{3(\hbar\pi)^2} \rightarrow \overline{P}_x = \frac{2}{3} \frac{\overline{E}}{V}$$

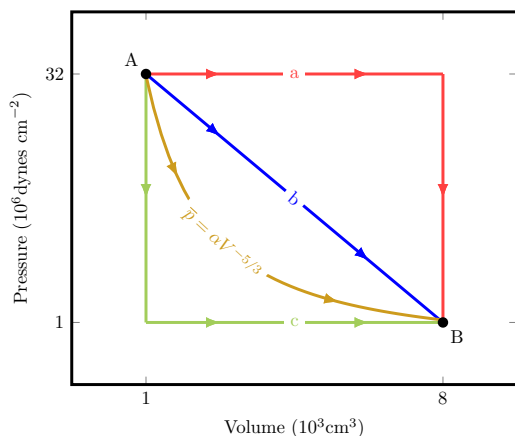
### 3 Homework 3

#### Problem 3.1 Reif 2.11

**REWRITE** In a quasi-static process  $A \rightarrow B$  in which no heat is exchanged with the environment, the mean pressure  $\bar{p}$  of a certain amount of gas is found to change with its volume  $V$  according to the relation:

$$\bar{p} = \alpha V^{-5/3}$$

where  $\alpha$  is a constant. Find the quasi-static work done and the net heat absorbed by the system in each of the following three processes, all of which take the system from macrostate  $A$  to macrostate  $B$ .



- The system is expanded from its original to its final volume, heat being added to maintain the pressure constant. The volume is then kept constant, and heat is extracted to reduce the pressure to  $10^{-6}$  dynes  $\text{cm}^{-2}$ .
- The volume is increased and heat is supplied to cause the pressure to decrease linearly with the volume.
- The two steps in process (a) are performed in the opposite order.

a)  $dW = p dV$  The quasi-static work done is the area under the curve, or:

$$W = 32(1 \times 10^6 \text{ dynes cm}^{-2}) * 7(1 \times 10^3 \text{ cm}^3) = 224 \times 10^9 \frac{\text{dynes}}{\text{cm}}$$

b) Again, the work is found through finding the area under the curve, only this time the shape is a trapezoid (my favorite shape!):

$$W = \frac{1 + 32}{2} (1 \times 10^6 \text{ dynes cm}^{-2}) \times (8 \times 10^3 \text{ cm}^3) = 1.32 \times 10^{11} \text{ dynes}$$

**Problem 3.2** *Reif 3.2*

Consider a system of  $N$  localized weakly-interacting particles, each of spin  $1/2$  and magnetic moment  $\mu$  located in an external magnetic field  $H$ .<sup>1</sup>

- (a) Using the expression for  $\ln(\Omega(E))$  calculated in Reif 2.4b and the definition  $\beta = \frac{\partial \ln \Omega}{\partial E}$  find the relation between the absolute temperature  $T$  and the total energy  $E$  of this system.
  - (b) Under what circumstances is  $T$  negative?
  - (c) The total magnetic moment  $M$  of this system is related to its energy  $E$ . Use the result of part (a) to find  $M$  as a function of  $H$  and the absolute temperature  $T$ .
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<sup>1</sup>This system was already discussed in Reif 2.4

**Problem 3.3** *Reif 3.4*

Suppose a system  $A$  is placed into thermal contact with a heat reservoir  $A'$  which is at an absolute temperature  $T'$  and that  $A$  absorbs an amount of heat  $Q$  in this process. Show that the entropy increase  $\Delta S$  of  $A$  in this process satisfies the inequality

$$\Delta S \geq \frac{Q}{T'}$$

Where the  $=$  case is only valid if the initial temperature of  $A$  differs infinitesimally from  $T'$ .

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**Problem 3.4** *Reif 3.5*

A system consists of  $N_1$  molecules of type 1, and  $N_2$  molecules of type 2 confined within a box of volume  $V$ . The molecules are supposed to interact very weakly so that they constitute an ideal gas mixture.

- (a) How does  $\Omega(E)$  (the total number of states between  $E, E + \delta E$ ) depend on  $V$  in this system? You may treat the problem classically.
  - (b) Use this result to find the equation of state of this system  $\rightarrow$  find the mean pressure  $\bar{p}$  as a function of  $V, T$ .
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## 4 Homework 4

### Problem 4.1 Reif 4.1

- (a) 1kg of water at 0°C is brought into contact with a large heat reservoir at 100°C. When the water has reached 100°C, what has been the change in entropy of the water? Of the heat reservoir? of the system that is the water and reservoir?
- (b) If the water has been heated 0°C → 100°C by instead first bringing it into contact with a 50°C reservoir, then with a 100°C reservoir, what would have been the change in the entropy of the entire system?
- (c) Show how the water might be heated 0°C → 100°C with no entropy change in the system.

- a) Using Reif Eqn. (4.5.2) assuming  $c_w = 4.2(\text{J}\cdot\text{kg}^{-1}\text{K}^{-1})$ ,  $m_w = 1000\text{g}$ :

$$\begin{aligned}
 \Delta S_w &\equiv S_w(373.16) - S_w(273.16) \\
 &= \int_{273.16}^{373.16} \frac{m_w c_w dT}{T} \\
 &= 4.18 \times 10^3 (\text{J}\cdot\text{K}^{-1}) \times \int_{273.16}^{373.16} \frac{dT}{T} \\
 &= 4.2 \times 10^3 (\text{J}\cdot\text{K}^{-1}) \times (\ln(373.16\text{K}) - \ln(273.16\text{K})) \\
 \Delta S_w &= 1310.19 \text{ J}\cdot\text{K}^{-1}
 \end{aligned}$$

For the reservoir:

$$\begin{aligned}
 Q_R &= -Q_w = -m_w c_w \Delta T = -1000 \times 4.18 \times 100 \\
 dS_R &= \frac{dQ}{T} = \frac{-m_w c_w \Delta T}{T} = \frac{-1000 \times 4.18 \times 100}{373} \\
 \Delta S_R &= -1120.64 \text{ J}\cdot\text{K}^{-1}
 \end{aligned}$$

So the total change in entropy for the system is  $\Delta S_{sys} = \Delta S_w + \Delta S_R = 189.55 \text{ J}\cdot\text{K}^{-1}$

- b)  $\Delta S_w$  is the same, but  $\Delta S_R$  is different:

$$\Delta S_R = -\left( \frac{m_w c_w 50}{323} + \frac{m_w c_w 50}{373} \right) = -1207.38 \text{ J}\cdot\text{K}^{-1}$$

So  $\Delta S_{sys} = 102.81 \text{ J}\cdot\text{K}^{-1}$

- c) If the temperature of the successive heat reservoirs is changed infinitesimally then there will be no change in entropy.

**Problem 4.2** *Reif 4.3*

The heat absorbed by a mole of ideal gas in a quasi-static process in which its temperature  $T$  changes by  $dT$  and its volume  $V$  by  $dV$  is given by

$$dQ = cdT + \bar{p}dV$$

where  $c$  is its constant molar specific heat at constant volume and  $\bar{p}$  is its mean pressure  $\bar{p} = RT/V$ . Find an expression for the change of entropy of this gas in a quasi-static process which takes it from  $(T_i, V_i) \rightarrow (T_f, V_f)$ . Does your answer depend on the process involved in going from the initial to the final state?

$$dQ = cdT + \frac{RT}{V}dV$$

$$dS = \frac{dQ}{T} = \frac{cdT}{T} + \frac{RdV}{V}$$

$$\Delta S = \int dS$$

$$= c \int_{T_i}^{T_f} \frac{dT}{T} + R \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Delta S = c \ln\left(\frac{T_f}{T_i}\right) + R \ln\left(\frac{V_f}{V_i}\right)$$

Since this depends on exact differentials  $dT, dV$  this is process independent.



**Problem 4.3** *Reif 5.2*

The molar specific heat at constant volume of a monatomic ideal gas is known to be  $\frac{3}{2}R$ . Suppose that one mole of such gas is subjected to a cyclic quasi-static process which appears as a circle on the  $P - V$  diagram on page 193. Find:

- (a) The net work (in Joules) done by the gas in one cycle.
- (b) The internal energy difference (in Joules) of the gas between states  $C$  and  $A$
- (c) The heat absorbed (in Joules) by the gas going from  $A \rightarrow C$  via the  $ABC$  path of the cycle.

- a)  $W = \int p dV$ , and due to the nature of the problem, the integral is equivalent to the area of the circle:  $\pi * 1^2 * \times 10^9 \text{ dynes} \cdot \text{cm}$ . Given that  $\times 10^9 \text{ dynes} \cdot \text{cm} \approx 100J$ , the answer can be written as:

$$W \approx 314 \text{ J}$$

- b) Since this is a state function and  $\nu = 1$ :

$$\begin{aligned} E &= \frac{3}{2}RT dE &= \frac{3}{2}RdT \\ \Delta E &= \frac{3R}{2}(T_A - T_C) \xrightarrow{T = \frac{pV}{R}} \Delta E = \frac{3}{2}(p_A V_A - p_C V_C) \\ &= \frac{3}{2}(2 * 1 - 2 * 3) \times 10^9 \text{ dynes} \cdot \text{cm} \end{aligned}$$

$$\Delta E_{AC} \approx 600J$$

- c)  $\Delta Q_{AC} = \Delta E_{CA} + \Delta W_{AC}$  part (a) found  $\Delta W$  for the full circle,  $W_{AC}$  is half of that plus the square under the circle. Part (b) found  $\Delta E_{AC}$ .

$$\Delta Q_{AC} = 600 + \left(400 + \frac{314}{2}\right)$$

$$\Delta Q_{AC} = 1157 \text{ J}$$

**Problem 4.4**

For an ideal gas whose entropy is fixed

$$E = kV^{-\frac{2}{3}}$$

where  $k$  is a constant independent of  $V$ .

- (a) Find an expression for the pressure  $p$  in terms of  $k$  and  $V$ .
- (b) Perform a Legendre transformation to find an appropriate function of  $P$  from which the same relation may be derived.

a)

$$dS = 0 = dQ \implies dQ = 0 = dE + pdV$$

$$dE = -pdV = \frac{\partial E}{\partial V} dV \implies -\frac{\partial E}{\partial V} = p$$

$$-\frac{\partial}{\partial V} (kV^{-2/3}) = \frac{2}{3}kV^{-5/3} = p$$

b) Why not rearrange algebraically?

$$0 = dE + pdV$$

$$0 = dE + pdV + Vdp - Vdp$$

$$0 = dE + d(pV) - Vdp$$

$$0 = d(E + pV) - Vdp$$

$$0 = dH - Vdp$$

$$dH = Vdp$$

???

**Problem 4.5**

The specific heat at constant volume and pressure are respectively:

$$C_V = \left( \frac{\partial Q}{\partial T} \right)_V, \quad C_P = \left( \frac{\partial Q}{\partial T} \right)_P$$

Present arguments that for an ideal gas ( $PV = NkT$ ,  $E = \frac{3}{2}NkT$ ):

$$dQ = C_V dT + PdV = C_P dT - VdP$$

For a quasistatic adiabatic process, show that the equation of state may be written, **using the above as**  $PV^\gamma = \text{Constant}$ . Where  $\gamma \equiv C_P/C_V$

$$C_p = T \left( \frac{\partial S}{\partial T} \right)_p = \left( \frac{T \partial S}{\partial T} \right)_p = \left( \frac{\partial Q}{\partial T} \right)_p \quad \checkmark$$

## 5 Homework 5

**Problem 5.1** *Reif 5.12*

$$m \frac{\Delta p}{\Delta T} \rightarrow m \left( \frac{\partial p}{\partial T} \right)_S \xrightarrow{D2} m \frac{-\left( \frac{\partial S}{\partial T} \right)_p}{\left( \frac{\partial S}{\partial p} \right)_T} \xrightarrow[M3]{C1} m \frac{C_p}{T \left( \frac{\partial V}{\partial T} \right)_p} \xrightarrow{C3} \frac{C_p}{T \alpha V} = \frac{\rho C_p}{T \alpha}$$

$$\frac{T \alpha}{\rho C_P} \Delta P = \Delta T$$

**Problem 5.2** *Reif 5.13*

A homogeneous substance at temperature  $T$  and pressure  $P$  has a molar volume  $V$  and a molar specific heat (measured at constant pressure) given by  $c_P$ . Its coefficient of volume expansion  $\alpha$  is known as a function of temperature. Calculate how  $c_P$  depends on the pressure at a given temperature. i.e. Calculate  $(\partial c_P / \partial p)_T$  in terms of  $T, V, \alpha$ .<sup>2</sup>

Making note that  $\alpha = \alpha(T)$

$$\begin{aligned}
 c_P &= T \left( \frac{\partial S}{\partial T} \right)_P \longrightarrow \left( \frac{\partial c_P}{\partial P} \right)_T = T \left[ \frac{\partial}{\partial P} \left( \frac{\partial S}{\partial T} \right)_P \right]_T = T \left[ \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial P} \right)_T \right]_P \xrightarrow{\frac{M3}{C3}} T \left[ \frac{\partial}{\partial T} (-\alpha V) \right]_P \\
 &= T \left( \frac{\partial V}{\partial T} \right)_P - VT \left( \frac{\partial \alpha}{\partial T} \right)_P \xrightarrow{C3} TV\alpha' - TV\alpha^2
 \end{aligned}$$

<sup>2</sup>For some reason Reif defines  $\alpha = -\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  in their solutions manual. The original definition  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$  is used here.

**Problem 5.3** *Reif 5.14*

See Reif pg. 196

(a)

$$\begin{aligned}
 TdS &= dQ = dE + dW \\
 &= dE - FdL \longrightarrow dE - aT^2(L - L_0)dL
 \end{aligned}$$

$$dS = \frac{dE}{T} - aT(L - L_0)dL$$

(b) Does constant E **imply** constant T, is that all we need?

$$\begin{aligned}
 dS &= \frac{1}{T} dE - aT(L - L_0) dL \\
 &= \left( \frac{\partial S}{\partial E} \right)_L dE + \left( \frac{\partial S}{\partial L} \right)_T dL \\
 \left( \frac{\partial S}{\partial L} \right)_T &= - \left( \frac{\partial F}{\partial T} \right)_L ??
 \end{aligned}$$

(c) what

$$\begin{aligned}
 S(T, L) - S(T_0, L_0) &= \int_{T_0}^{T_f} \frac{1}{T} dE - aT \int_{L_0}^L (L' - L_0) dL' \\
 S(T, L) &= \int_{T_0}^{T_f} \frac{b}{C_L} dE - aT \left( \frac{L^2}{2} - \frac{L_0^2}{2} - LL_0 + L_0^2 \right) \\
 &= \int_{T_0}^{T_f} \frac{b}{T \left( \frac{\partial S}{\partial T} \right)_L} dE - aT \frac{1}{2} (L^2 + L_0^2 - 2LL_0) \\
 &= \int_{T_0}^{T_f} \frac{1}{bT \left( \frac{\partial Q}{\partial T} \right)_L} dE - \frac{aT}{2} (L - L_0)^2
 \end{aligned}$$

**Problem 5.4** *Crushing*  $(T/V)_H$ 

Crush the derivative  $(\frac{\partial T}{\partial V})_H$  and write it in terms of  $C_p, \kappa, \alpha, V, T$ .

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$$\left(\frac{\partial T}{\partial V}\right)_H \xrightarrow{D2} \frac{-\left(\frac{\partial H}{\partial V}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_V}$$

## 6 Homework 6

**Problem 6.1** *Reif 5.15*

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**Problem 6.2** *Reif 5.17*

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**Problem 6.3** *Reif 5.23*

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## 7 Homework 7

**Problem 7.1** *Reif 5.26*

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**Problem 7.2**

The thermodynamic variables for a magnetic system are  $H, M, T$  where  $H$  is the magnetic field,  $M$  is the magnetization and  $T$  the absolute temperature. The magnetic work is  $dW = -HdM$  and the first law states that  $dE = TdS + HdM$ . The equation of state is given by Curie's law,  $M = \kappa H/T$  where  $\kappa$  is a constant. The heat capacity at constant  $H$  is  $C_H$ , and at constant  $M$  is denoted by  $C_M$ . Many thermodynamic relations can be obtained from those of the  $P, V, T$  system by the correspondence  $H \leftrightarrow -P$ ,  $M \leftrightarrow V$ .

(a) Show that  $C_M = \left( \frac{\partial E}{\partial T} \right)_M$  and that  $C_H = \left( \frac{\partial E}{\partial T} \right)_H - H \left( \frac{\partial M}{\partial T} \right)_H$

(b) Using Curie's law and the first law show that

$$\left( \frac{\partial E}{\partial M} \right)_T = 0$$

(c) Show that

$$C_H - C_M = \frac{M^2}{k}$$

**Problem 7.3**

Later on in the course we will see that the equation of state of radiation is:  $pV = E/3$ . Stefan's law relates the energy to the temperature and volume by:  $E = \sigma VT^4$  where  $\sigma$  is a constant. Using just this, answer the following:

- (a) Find the entropy  $S$  of radiation as a function of  $V, T$ .<sup>3</sup>
- (b) During the big bang, radiation initially confined to a small region expands adiabatically and cools down. Using the result of part (a) find the relationship between the temperature  $T$  and radius of the universe  $R$ .

**8 Homework 8****9 Homework 9****10 Homework 10**

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<sup>3</sup>Hint: use the fact that  $dS$  is an exact differential and therefore path independent.

## 11 Homework 11

**Problem 11.1** *Reif 8.2*

The vapor pressure  $P$  (in mmHg) of solid ammonia is given by

$$\ln(P) = 23.03 - \frac{3754}{T}$$

and liquid ammonia is

$$\ln(P) = 19.49 - \frac{3063}{T}$$

- (a) What is the temperature of the triple point?
- (b) What are the latent heats of sublimation and vaporization at the triple point?
- (c) What is the latent heat of melting at the triple point?

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- a) find  $T$  that makes two eqns equal  $T = 195.2K$
  - b) Formula in textbook 3.121E4J
  - c)  $l_{\text{sub-lvap}}=5.74\text{E}3\text{J}$

**Problem 11.2** *Reif 8.11*

Consider a classical ideal gas in thermal equilibrium at temperature  $T$  in a container of volume  $V$  in the presence of a uniform gravitational field. The acceleration due to gravity is  $g$  and is oriented in the  $-z$  direction.

- (a) Calculate the chemical potential  $\mu$  of an element of volume of such a gas as a function of the pressure  $P$ , temperature  $T$ , and height  $z$ .
- (b) Show that the requirement that  $\mu$  is constant implies immediately the law of atmospheres which gives the dependence on  $P, T, z$ .

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a)  $\mu = \left(\frac{\partial F}{\partial N}\right)_{TV}$  and  $F = E - TS = (E_0 + E_N) - T(S_0 + S_N)$  eqn 7.35

b)  $P(z) = P(0)\exp\left(\frac{-mg}{kT}z\right)$