

6CCP3212 Statistical Mechanics Homework 1

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<https://nms.kcl.ac.uk/eugene.lim/teach/statmech/sm.html>

1) (i) For the following differentials with α and β non-zero real constants, which are exact and which are inexact? Integrate the equation if it is exact.

(a)

$$dG = \alpha dx + \beta \frac{x}{y} dy \quad (1)$$

(b)

$$dG = \frac{\alpha}{x} dx + \beta dy \quad (2)$$

(c)

$$dG = (x + y)dx + \frac{x^2}{2} dy \quad (3)$$

(ii) Show that the work done on the system at pressure P

$$dW = -PdV \quad (4)$$

where dV is the change in volume is an inexact differential by showing that there exists no possible function of state for $W(P, V)$.

(iii) Consider the differential

$$dF = (x^2 - y)dx + xdy . \quad (5)$$

(a) Show that this is not an exact differential. And hence integrate this equation in two different *straight* paths from $(1, 1) \rightarrow (2, 2)$ and from $(1, 1) \rightarrow (1, 2) \rightarrow (2, 2)$, where (x, y) indicates the locations. Compare the results – are they identical?

(b) Define a new differential with

$$dG \equiv \frac{dF}{x^2} = \left(1 - \frac{y}{x^2}\right) dx + \frac{1}{x} dy . \quad (6)$$

Show that dG is exact, and find $G(x, y)$.

2) This problem asks you to derive some derivative identities of a system with three variables x , y and z , with a single constraint $x(y, z)$. This kind of system is central to thermodynamics as we often use three state variables P , V and T , with an equation of state $P(V, T)$ (i.e. the constraint) to describe a system.

(i) Prove the following identity

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \quad (7)$$

and hence show that for any equation of state $P(V, T)$ with the state variables P , V and T , the partial derivatives are related by

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1 . \quad (8)$$

(ii) Suppose $f(x, y)$ is a function of x, y . Since there exists a constraint $x(y, z)$, we can invert this to become $y(x, z)$, and hence execute a coordinate transform $f(x, y) \rightarrow f(x, z)$. Show that the following identity holds in this case

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z . \quad (9)$$

This identity allows us to go from the partial derivatives of one set of state variables to another as long as we know the equation of state.

3) The heat capacities for constant pressure and constant volume as discussed in class are given by

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V, \quad C_P = T \left(\frac{\partial S}{\partial T} \right)_P. \quad (10)$$

(i) Show that they can be expressed as

$$C_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V, \quad C_P = -T \left(\frac{\partial^2 \Phi}{\partial T^2} \right)_P, \quad C_P = \left(\frac{\partial H}{\partial T} \right)_P. \quad (11)$$

(ii) Show that the derivative of C_V is given by

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V, \quad (12)$$

hence once an equation of state $P(V, T)$ is known, then this can be easily calculated.

(iii) Consider the entropy $S(P, T)$, such that

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT. \quad (13)$$

Using the result of Q2, perform the coordinate transform from $S(P, T) \rightarrow S(T, V)$ to show that

$$dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left[\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial S}{\partial P} \right)_T + \left(\frac{\partial S}{\partial T} \right)_P \right] dT \quad (14)$$

hence

$$\left(\frac{\partial S}{\partial T} \right)_V = \left[\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial S}{\partial P} \right)_T + \left(\frac{\partial S}{\partial T} \right)_P \right]. \quad (15)$$

Using this result, prove that the difference between the two heat capacities is

$$\frac{C_P - C_V}{T} = \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V. \quad (16)$$

Check that for an ideal gas with equation of state $PV = Nk_bT$, this relationship gives the familiar result $C_P - C_V = Nk_b$.

4) The **Compressibility** of a system is defined by

$$K_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (17)$$

for constant T (or *isothermal*) compression, and

$$K_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S \quad (18)$$

for constant S (or *adiabatic*) compression. The compressibility measures how much volume ΔV is increased/reduced when the pressure is increased/decreased, for either fixed T or S .

Consider a gas immersed in a heat bath of temperature T , with two sections of volume V_1 and V_2 separated by a movable partition – see Fig. 1.

(i) Show by rescaling that the compressibility is an *intensive* quantity.

(ii) Suppose the system begins in equilibrium with total entropy $S = S_1 + S_2$ and energy $E = E_1 + E_2$. By moving the partition *adiabatically*, we can increase/decrease the volumes V_1 and V_2 while keeping the total volume V , the total energy E and the total entropy S fixed i.e. keeping the total system in equilibrium. However, since the two partitions' volumes V_1 and V_2 are changing, each partition is free to

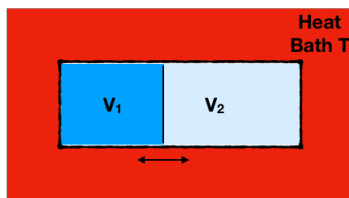


Figure 1: Figure for Problem 4

find their own equilibria at constant T . Let F_1 and F_2 be the Helmholtz free energies for the partitions. Show that the total free energy of the system is additive

$$F = F_1 + F_2 , \quad (19)$$

and that the total F is a constant when we move the partition adiabatically, thus

$$\frac{\partial F}{\partial V_1} = \frac{\partial F}{\partial V_2} = 0 . \quad (20)$$

Hence show that

$$\frac{\partial F}{\partial V_1} = \frac{\partial F_1}{\partial V_1} - \frac{\partial F_2}{\partial V_2} = 0 . \quad (21)$$

(Hint : By take the total derivative of $V = V_1 + V_2$ and using the conservation of V , we can derive the Jacobian

$$\frac{dV_1}{dV_2} = -1 , \quad (22)$$

which will be useful for the last part of this question.)

(iii) In class, we argued that at equilibrium F is a *minimum*. This means that

$$\frac{\partial^2 F}{\partial V_1^2} > 0 . \quad (23)$$

Use the results of section (i) and the definitions of compressibility to show that

$$\frac{1}{V_1(K_T)_1} + \frac{1}{V_2(K_T)_2} > 0 \quad (24)$$

in general. Since the partitions contain identical gases and K_T is intensive, this means that $(K_T)_1 = (K_T)_2$, and hence this proves that compressibility is *always positive* $K_T > 0$ in general. Thus prove that

$$\left(\frac{\partial P}{\partial V} \right)_T < 0 , \quad (25)$$

in general. (See section 5.2 of the lecture notes for a physical explanation why this inequality is a general result.)

(iv) Using the results of Q2 and Q3, show that

$$C_P - C_V = TVK_T \left(\frac{\partial P}{\partial T} \right)_V^2 . \quad (26)$$

If $T \geq 0$, then this implies that $C_P \geq C_V$.

5) Consider a rod of initial length L_0 and temperature T_0 . At temperature T and length L , the tension force f of the rod is given by

$$f = aT^2(L - L_0) \quad (27)$$

where $a > 0$ is a positive definite constant. One can think of this as a thermodynamic system with two state variables T and L , where L plays the role of volume V , and f plays the role of pressure P hence the above is an equation of state.

(i) Argue that the fundamental equation of thermodynamic for this system is given by

$$dE = TdS + fdL . \quad (28)$$

Why is the work term $dW = fdL$ positive?

(ii) Show that the equivalent Maxwell relation for this system is

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L . \quad (29)$$

Compare it the usual $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, we have gained a $-$ sign. Can you see why?

(iii) At $L = L_0$, we heat up the rod (i.e. $dQ > 0$), and make a measurement of the heat capacity at fixed length C_L , to find that it is $C_L(L_0) = bT$. Use your results in (ii), show that the entropy of the system S in terms of L and T is given by

$$S(L, T) = S(L_0, T_0) + b(T - T_0) - aT(L - L_0)^2 . \quad (30)$$

(Hint : Integrate $S(L, T)$ separately by fixing L_0 and then T_0 .)

(iv) Finally, show that

$$\left(\frac{\partial C_L}{\partial L}\right)_T = -2aT(L - L_0) \quad (31)$$

and hence calculate the heat capacity of the system as a function of T and L .

(v) If we adiabatically stretches the rod, keeping the rod in thermally isolated, does the temperature of the rod increase or decrease?

6) Consider an ideal gas with equation of state $PV = Nk_bT$ of fixed N , and with a constant heat capacity $C_V = Nk_b\alpha$, where $\alpha > 0$ being a real positive definite constant.

(i) By considering a change of variables from $E(V, S) \rightarrow E(V, T)$, use the identity of Q2 to show that

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \quad (32)$$

Use this relationship to prove that for an ideal gas with equation of state of $PV = Nk_bT$,

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 , \quad (33)$$

implying that E is independent of V . As we will discuss further in Chapter 2, an ideal gas is a gas whose particles do not interact with each other – this means that its total internal energy does not depend on the gas density since there is no interaction energy, and hence it makes sense that E is independent of V .

(ii) Use the results of Q3 to show that

$$C_P = Nk_b(\alpha + 1) . \quad (34)$$

(iii) Use the fundamental equation of thermodynamics to prove that

$$S = Nk_b \ln V + Nk_b\alpha \ln T + \text{const} . \quad (35)$$

(iv) In a reversible (adiabatic) process, $dS = 0$. In this case, using $\gamma \equiv C_P/C_V$, prove the following familiar results

$$VT^\alpha = \text{const} \Rightarrow TV^{\gamma-1} = \text{another const} \quad (36)$$

and,

$$PV^\gamma = \text{const} . \quad (37)$$

7) (The **Carnot Cycle**, Fig. 2). An *engine* is a thermodynamic system which extracts heat Q_1 from a reservoir T_1 , do work W , and then dumps the waste heat Q_2 in to a heat sink $T_2 < T_1$. Via conservation of energy, the total work done *on* the engine $W = Q_2 - Q_1$. (Note the negative, since we get net work out of the engine.) The Carnot cycle is a thermodynamic engine which is reversible. It consists of 4

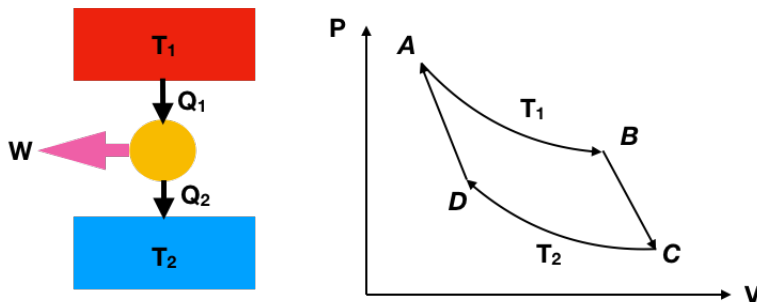


Figure 2: Problem 7 : Carnot Cycle

phases: (a) AB (isothermal expansion at T_1) where heat Q_1 is extracted from the heat reservoir (b) BC (adiabatic expansion) where work is done by the engine (c) DC (isothermal compression at T_2) where the waste heat Q_2 is discarded to the heat sink (d) CA (adiabatic compression) where work is done on the engine.

(i) Since the system is reversible, the total entropy S remains constant. Show that this gives us the relationship

$$Q_2 = \frac{Q_1 T_2}{T_1} , \quad (38)$$

and hence show that in a *irreversible* engine, this leads to the inequality

$$Q_2 > \frac{Q_1 T_2}{T_1} . \quad (39)$$

(ii) If we define the *efficiency* of an engine to be

$$\eta \equiv \frac{|W|}{Q_1} \quad (40)$$

then use your results from (i) to show that

$$\eta \leq \frac{T_1 - T_2}{T_1} \quad (41)$$

and hence argue that the Carnot cycle is the most efficient engine theoretically possible.

(iii) Use the results of Q6(iv) to show that

$$\frac{V_A}{V_B} = \frac{V_D}{V_C} . \quad (42)$$

(iv) Specializing to the case where we use an ideal gas with the equation state $PV = Nk_b T$ for the engine. Using $dQ = -dW = PdV$, show that the isothermal expansion AB obeys

$$Q_1 = Nk_b T_1 \ln \frac{V_B}{V_A} , \quad (43)$$

and that the isothermal compression CD obeys

$$Q_2 = Nk_bT_2 \ln \frac{V_D}{V_C} . \quad (44)$$

And hence show that the Clausius equality

$$\oint \frac{dQ}{T} = 0 \quad (45)$$

is obeyed.

8) Show that for processes at constant pressure and temperature, the Gibbs free energy evolves in time as

$$\frac{d\Phi}{dt} < 0 . \quad (46)$$

9) The Van der Waals equation of state describes a gas which is weakly interacting at long distances (we will derive this equation of state in Chapter 3), and is given by

$$P = \frac{k_bT}{V/N - b} - \frac{N^2}{V^2}a \quad (47)$$

where a and b are constants. Consider a Van der Waals gas, with fixed N .

(i) Show that setting $a = b = 0$ recovers the ideal gas equation of state.

(ii) By considering $E(V, T)$, show that the differential dE for a Van der Waals gas is

$$dE = C_V dT + \frac{N^2}{V^2} a dV . \quad (48)$$

(Hint : use the identity you derived in Q6(i)).

(iii) Show that the heat capacity is independent of V and only dependent on T , i.e. $C_V(T)$. (Hint: Use the identities derived in Q3.)

(iv) By considering $S(T, V)$ show that the differential dS for a Van der Waals gas is

$$dS = \frac{C_V}{T} dT + \frac{k_b}{V/N - b} dV . \quad (49)$$

(v) Finally, assuming that C_V is also independent of time, i.e. $C_V = \text{const}$, then the energy and entropy is given by

$$E = C_V T - \frac{aN^2}{V} + \text{constant} , \quad (50)$$

and

$$S = C_V \ln T + Nk_b \ln \left(\frac{V}{N} - b \right) + \text{const} . \quad (51)$$

Comparing this result to that of an ideal gas you derived in Q6, the energy E for the Van der Waals gas is dependent on V – why?