6CCP3212 Statistical Mechanics Solutions 1

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1) (i) (a) We can rewrite the differential as $dG = \alpha dx + \beta x d(\ln y)$, and hence

$$\left(\frac{\partial G}{\partial x}\right)_y = \alpha \to G = \alpha x + f(y) \tag{1}$$

while

$$\left(\frac{\partial G}{\partial \ln y}\right)_x = \left(\frac{\partial f(y)}{\partial \ln y}\right)_x = \beta x \to G = \beta x \ln y + \alpha x \tag{2}$$

but these are inconsistent so not exact.
(b)

$$\left(\frac{\partial G}{\partial x}\right)_y = \alpha/x \to G = \alpha \ln x + f(y) \tag{3}$$

and

$$\left(\frac{\partial G}{\partial y}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x = \beta \to f(y) = \beta y + \text{const} \tag{4}$$

hence $G(x,y) = \alpha \ln x + \beta y + \text{const}$ so exact.
(c) From

$$\left(\frac{\partial G}{\partial x}\right)_y = x + y \to G = \frac{x^2}{2} + xy + f(y) \tag{5}$$

while

$$\left(\frac{\partial G}{\partial y}\right)_x = \left(\frac{\partial f}{\partial y}\right)_x + x = \frac{x^2}{2} \tag{6}$$

but $f(y)$ constains no x so is inconsistent hence this is inexact.
Trick: A differential $dG = A(x,y)dx + B(x,y)dy$ is exact when it obeys the following

$$\frac{\partial A(x,y)}{\partial y} = \frac{\partial B(x,y)}{\partial x} \tag{7}$$

so you can also use it to check for exactness quickly. (You still need to integrate if it is exact.)
(ii) Using the methods above

$$\left(\frac{\partial W}{\partial V}\right)_P = -P \to W = -PV + f(P) \tag{8}$$

and

$$\left(\frac{\partial W}{\partial P}\right)_V = -V + \left(\frac{\partial f}{\partial P}\right)_V = 0 \tag{9}$$

but for the 2nd term to cancel $-V$, $f(P)$ must contain V which contradicts, hence W is not exact.
(iii) (a) From

$$\left(\frac{\partial F}{\partial x}\right)_y = x^2 - y \to \frac{x^y}{3} - yx + f(y) \tag{10}$$

and

$$\left(\frac{\partial F}{\partial y}\right)_x = -x + \left(\frac{\partial f(y)}{\partial y}\right)_x = x \tag{11}$$

and since $f(y)$ contains no x this cannot be true hence not exact.

Since it is not exact, we have to be careful when we do the integration along the paths. Let's call path $(1,1) \to (1,2) \to (2,2)$ path A and path $(1,1) \to (2,2)$ path B.

- Path A : We can split the integral into the constant x and constant y paths so

$$\int_A dF = \int_{(1,1)}^{(1,2)} dF + \int_{(1,2)}^{(2,2)} dF = \int_1^2 dy + \int_1^2 (x^2 - 2)dx = -1 + \frac{7}{3} \ . \tag{12}$$

- Path B : We want to integrate along the straight line $y = x$ from $(1,1) \to (2,2)$. To do this line integral, we want to express the path as a function of some parameter t. It's easy to see that such a parameterization is given by

$$x(t) = t \ , \ y(t) = t \text{ for } 1 \leq t \leq 2 \ . \tag{13}$$

  Then $dx = dy$, $dy = dt$, and the integral becomes

$$\int_B dF = \int_{t=1}^{t=2} (x^2(t) - y(t) + x(t))dt = \int_1^2 t^2 dt = \frac{7}{3} \ . \tag{14}$$

And hence we have shown that an inexact differential yields different values depending on its paths.
(b) $G(x,y) = x + y/x + \text{constant}$.

2) (i) Since we have a constraint $x(y,z)$ this means that we can also invert $y(x,z)$ thus

$$\begin{aligned} dx &= \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \\ &= \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] + \left(\frac{\partial x}{\partial z}\right)_y dz \\ &= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz \end{aligned} \tag{15}$$

But the first term is just dx, so the second bracketed term must vanish, or

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0 \to \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \ . \blacksquare \tag{16}$$

and hence we are done. Substituting $x = V$, $y = T$, $z = P$, we get the second relationship.
(ii) From $f(x,y)$, we have

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{17}$$

But since there is a constraint $y(x,z)$, this allows to express

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz \tag{18}$$

and plugging this into df we have

$$\begin{aligned} df &= \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz\right] \\ &= \left[\left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z\right] dx + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial z}\right)_x dz \end{aligned} \tag{19}$$

and, interpreting the above result as $f(x,z)$ this means that

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \ . \blacksquare \tag{20}$$

3)

(i) Use $S = -\left(\frac{\partial F}{\partial T}\right)_V$ and $S = -\left(\frac{\partial \Phi}{\partial T}\right)_P$, plug in to get

$$C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V \;,\; C_P = -T\left(\frac{\partial^2 \Phi}{\partial T^2}\right)_V \tag{21}$$

From $H = TdS + VdP$, we have

$$T = \left(\frac{\partial H}{\partial S}\right)_P \tag{22}$$

then using $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$ we get

$$C_P = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \;. \blacksquare \tag{23}$$

(ii) From

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial}{T\partial V}\left(\left(\frac{\partial S}{\partial T}\right)_V\right)_T \tag{24}$$

but since dS is exact, we can use the trick described in the solution to Q1 to flip the derivatives around

$$\frac{\partial}{\partial V}\left(\left(\frac{\partial S}{\partial T}\right)_V\right)_T = \frac{\partial}{\partial T}\left(\left(\frac{\partial S}{\partial V}\right)_T\right)_V \tag{25}$$

and then use the Maxwell relation $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ to get

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \;. \blacksquare \tag{26}$$

(iii) The first part of the problem is a direct application of the identities of Q2ii, with $f(x,y) \to f(x,z)$ replaced by $S(T,P) \to S(T,V)$. Then we have

$$\begin{aligned} \frac{C_P - C_V}{T} &= \left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V \\ &= -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial S}{\partial P}\right)_T \end{aligned} \tag{27}$$

and using the Maxwell relation $-\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$ we are done. $\blacksquare$

4)

(i) It is easy to see that under linear rescaling with $a > 0$, $V \to aV$ and $P \to P$, $K \to K$.

(ii) From $F_1 = E_1 - TS_1$, and $F_2 = E_2 - TS_2$, we have $F_1 + F_2 = (E_1 + E_2) - T(S_1 + S_2) = E - TS = F$. Taking derivative

$$\frac{\partial F}{\partial V_1} = \frac{\partial F_1}{\partial V_1} + \frac{\partial F_2}{\partial V_1} = \frac{\partial F_1}{\partial V_1} + \frac{\partial V_2}{\partial V_1}\frac{\partial F_2}{\partial V_2} = \frac{\partial F_1}{\partial V_1} - \frac{\partial F_2}{\partial V_2} = 0 \;, \tag{28}$$

since F is conserved.

(iii) Taking the 2nd derivative of F w.r.t. V_1, we get

$$\frac{\partial^2 F}{\partial V_1^2} = \frac{\partial^2 F_1}{\partial V_1^2} + \frac{\partial^2 F_2}{\partial V_2^2} > 0 \tag{29}$$

but using

$$P_i = -\left(\frac{\partial F_i}{\partial V_i}\right)_T \tag{30}$$

so

$$\left(\frac{\partial P_i}{\partial V_i}\right)_T = -\left(\frac{\partial^2 F_i}{\partial V_i^2}\right)_T \tag{31}$$

and then using the definition for K_T we get

$$\frac{1}{V_1 (K_T)_1} + \frac{1}{V_2 (K_T)_2} > 0 \;, \tag{32}$$

as requested, and hence $K_T > 0$ in general.
(iv) From Q3, we have

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V \tag{33}$$

but from Q2 we have

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V K_T V \tag{34}$$

and hence we get the required answer

$$C_P - C_V = TVK_T\left(\frac{\partial P}{\partial T}\right)_V^2 . \blacksquare \tag{35}$$

5) As the question indicated, the way to think about this rod as a thermodynamic system is to make the connection that $f = aT^2(L - L_0)$ is an equation of state with 3 state variables, T, L, and f (you can think of L and f as V and P analogues if you like).
(i) The 1st law is

$$dE = đQ + đW . \tag{36}$$

Using the definition of entropy, we have $đQ = TdS$. But now work done on the system is the usual Force $\times$ Length, equation $đW = fdL$. It is positive because as to stretch the system, we need to apply force – to increase L we need to increase f (unlike gasses, where we need to decrease V to increase P.)
(ii) This change in sign will mean that, from the definition of the Helmholtz free energy $F = E - TS$

$$dF = dE - TdS - SdT = -SdT + fdL \tag{37}$$

and hence

$$S = -\left(\frac{\partial F}{\partial T}\right)_L , \; f = \left(\frac{\partial F}{\partial L}\right)_T \tag{38}$$

(notice the sign difference) and thus

$$\left(\frac{\partial f}{\partial T}\right)_L = \frac{\partial}{\partial T}\left(\left(\frac{\partial F}{\partial L}\right)_T\right)_L = \frac{\partial}{\partial L}\left(\left(\frac{\partial F}{\partial T}\right)_L\right)_T = -\left(\frac{\partial S}{\partial L}\right)_T . \tag{39}$$

(iii) From $S(L,T)$, so

$$dS = \left(\frac{\partial S}{\partial L}\right)_T dL + \left(\frac{\partial S}{\partial T}\right)_L dT = \left(\frac{\partial S}{\partial L}\right)_T dL + \frac{C_L}{T}dT . \tag{40}$$

Using results from (ii) we note

$$\left(\frac{\partial S}{\partial L}\right)_T = -2aT(L - L_0) \tag{41}$$

so integrating for L along fixed T_0

$$S(L,T) - S(L,T_0) = \int_{L_0}^{L}\left(\frac{\partial S}{\partial L}\right)_T dL = \int_{L_0}^{L} -2aT(L - L_0)dL = -aT(L - L_0)^2 . \tag{42}$$

Meanwhile integrating for T along fixed L_0, we have

$$S(L,T) - S(L_0,T) = \int_{T_0}^{T}\frac{C_L(L_0)}{T}dT = \int_{T_0}^{T} bdT = b(T - T_0) \tag{43}$$

and hence the entropy is

$$S(L,T) = S(L_0,T_0) + b(T - T_0) - aT(L - L_0)^2 \tag{44}$$

(iv) We already know that the heat capacity at L_0 is $C_L(L_0, T) = bT$. We now want to calculate the heat capacity at fixed T. To do this, note that

$$\begin{aligned}
\left(\frac{\partial C_L}{\partial L}\right)_T &= \frac{\partial}{\partial L}\left(T\left(\frac{\partial S}{\partial T}\right)_L\right)_T \\
&= T\frac{\partial}{\partial T}\left(\left(\frac{\partial S}{\partial L}\right)_T\right)_L \\
&= T\frac{\partial}{\partial T}(-2aT(L-L_0)) \\
&= -2aT(L-L_0)
\end{aligned} \tag{45}$$

Then integrating along fixed T we have

$$C_L(L,T) = bT + \int_{L_0}^{L} -2aT(L-L_0)dL = bT - aT(L-L_0)^2 \ . \tag{46}$$

(v) If we adiabatically stretches the rod, S remains constant since there is no change in entropy, we have from (iii)

$$\text{constant} + b(T - T_0) = aT(L-L_0)^2 \tag{47}$$

Then if we increase $L > L_0$, the RHS will increase, and the LHS must also increase. Thus since $b > 0$ (the rod is in tension, not compression), then T must also increase.

6)

(i) Using the identity of Q2, with $f \to E$, $x \to V$, $y \to S$ and $z \to T$, we get

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_S + \left(\frac{\partial E}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T \tag{48}$$

But now from the fundamental equation $dE = TdS - PdV$, i.e.

$$\left(\frac{\partial E}{\partial S}\right)_V = T \ , \ \left(\frac{\partial E}{\partial V}\right)_S = -P \tag{49}$$

gets us

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T\left(\frac{\partial S}{\partial V}\right)_T \ , \tag{50}$$

and then using the Maxwell relation $(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V$

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \ ., \tag{51}$$

as required. Using the ideal gas equation of state $P = Nk_bT/V$, $(\frac{\partial P}{\partial T})_V = P$, and thus

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \ . \tag{52}$$

(ii) From Q3(iii), we have

$$\frac{C_P - C_V}{T} = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \tag{53}$$

and using $V = Nk_bT/P$, $(\frac{\partial V}{\partial T})_P = Nk_b/P$ and $(\frac{\partial P}{\partial T})_V = Nk_b/V$, and $C_V = Nk_b\alpha$ we get the final answer

$$C_P = Nk_b(\alpha + 1) \tag{54}$$

(iii) First express the differential $E(T, V)$ as

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = \left(\frac{\partial E}{\partial T}\right)_V dT \tag{55}$$

since the 2nd term vanishes from (i). Now from the fundamnetal equation

$$\begin{aligned} dS &= \frac{1}{T}dE + \frac{P}{T}dV \\ &= \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \frac{Nk_b}{V}dV \\ &= \frac{C_V}{T}dT + \frac{Nk_b}{V}dV \ . \end{aligned} \tag{56}$$

Integrating this equation, we get

$$S(T,V) = \int Nk_b\alpha d\ln T + \int Nk_b d\ln V = Nk_b\alpha\ln T + Nk_b\ln V + \text{const} \ .\blacksquare \tag{57}$$

(iv) From (iii) and setting $dS = 0$, we have

$$-\frac{\alpha}{T}dT = \frac{1}{V}dV \to VT^\alpha = \text{const} \tag{58}$$

and now using $C_P/C_V = (\alpha+1)/\alpha = \gamma$, we get the adiabatic relationship $TV^{\gamma-1}$. Plugging $T = PV/Nk_b$, we get $PV^\gamma = \text{const}$.

7)

(i) The phases are reversible as it is a Carnot cycle. There are two moments when the entropy is change which is the two isothermal phases at T_1 and T_2, with Q_1 and Q_2 being transfered.

$$đS_i = \frac{đQ_i}{T_i} \to \Delta S_i = \frac{\Delta Q_i}{T_i} \tag{59}$$

since T_i is constant. Thus

$$\Delta S = \Delta S_1 + \Delta S_2 = 0 \to \frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0 \tag{60}$$

and hence

$$Q_2 = \frac{Q_1 T_2}{T_1} \ . \tag{61}$$

In an irreversible engine, some heat is lost due to inefficiencies, so the actual work done $W < |Q_2 - Q_1|$, and hence $Q_2^{irrev} > Q_2^{rev}$ (more heat wasted into the sink), so

$$Q_2 > \frac{Q_1 T_2}{T_1} \ . \tag{62}$$

(Note that this leads directly to the Clausius Inequality.)

(ii) In a reversible (Carnot) engine, $|W| = Q_2 - Q_1$, so this leads directly to

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \ . \tag{63}$$

For a irreversible engine, this leads to the inequality

$$\eta < \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \ . \tag{64}$$

(iii) Using $TV^{\gamma-1} = \text{const}$, we have for the adiabatic phase $B - C$, $T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1}$, and similarly for the adiabatic phase $D - A$, we have $T_2 V_D^{\gamma-1} = T_1 V_A^{\gamma-1}$, and hence canceling the temperatures

$$\frac{V_A}{V_B} = \frac{V_D}{V_C} \tag{65}$$

(iv) In an adiabatic expansion, $đQ = PdV = Nk_bT/V dV$, hence for the heat extraction phase $A - B$

$$Q_1 = \int_B^A \frac{Nk_b T_1}{V}dV = Nk_b T_1 \ln\frac{V_B}{V_A} \tag{66}$$

and for heat disposal phase $D - C$

$$Q_2 = \int_D^C \frac{Nk_bT_2}{V} dV = Nk_bT_2 \ln \frac{V_D}{V_C} \ . \tag{67}$$

The loop integral is then

$$\oint \frac{đQ}{T} = Nk_b \left[\ln \frac{V_B}{V_A} + \ln \frac{V_D}{V_C} \right] = Nk_b \left[-\ln \frac{V_A}{V_B} + \ln \frac{V_D}{V_C} \right] 0 \tag{68}$$

via the results from (iii).

8) From the first law we have

$$\frac{dE}{dt} + P\frac{dV}{dt} < T\frac{dS}{dt} \tag{69}$$

and rewriting

$$\frac{dE}{dt} + P\frac{dV}{dt} - T\frac{dS}{dt} < 0 \ . \tag{70}$$

Since P and T is constant in time, we can bring them into the derivative to get

$$\frac{d}{dt}(E + PV - TS) = \frac{d\Phi}{dt} \tag{71}$$

hence

$$\frac{d\Phi}{dt} < 0 \ . \tag{72}$$

So the Gibbs free energy is minimum at equilibrium.

9) (i) Trivial.
(ii) Given $E(V, T)$, then

$$dE = \left(\frac{\partial E}{\partial V}\right)_T dT + \left(\frac{\partial E}{\partial T}\right)_V dV \tag{73}$$

The second term is just $C_V = \left(\frac{\partial E}{\partial T}\right)_V$, but the first term we use the identity from Q6

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V = -P + \frac{k_bT}{V/N - b} = \frac{N^2}{V^2}a \ . \tag{74}$$

(iii) If C_V is independent of V then $\partial C_V/\partial V = 0$. Using the identity from Q3(ii), we have

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0 \ . \tag{75}$$

(iv) From $S(T, V)$ we get

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \ . \tag{76}$$

The first term comes from the definition of $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$, and the second term we use the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{k_b}{V/N - b} \tag{77}$$

and hence the final answer.
(v) Assuming that C_V is also independent of T this means that $C_V = \text{const}$. We can then integrate for the entropy

$$\begin{aligned} \int dS = S &= \int \frac{C_V}{T} dT + \int \frac{k_b}{V/N - b} dV \\ &= C_V \ln T + Nk_b \ln\left(\frac{V}{N} - b\right) + \text{const} \ , \end{aligned} \tag{78}$$

and the energy

$$\int dE = E = \int C_V dT + \frac{N^2}{V^2} a dV$$
$$= C_V T - \frac{N^2}{V} a + \text{const} \; . \tag{79}$$

The energy now depends on the V, and hence the density. This is not surprising since the Van der Waals equation of state describes systems with particles with a long range interaction, and hence contribute interaction energy $V \times \rho$, with $\rho = N/V$. The negative sign means that the Van der Waals interaction is *attractive* in long ranges.