

Thermodynamics

Solution to selected problems of Reichl's

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- Answer to problem 2.13

The total work performed by the magnetic field to produce a material magnetization M provides the internal energy of the paramagnetic system

$$\bar{d}Q = dU + \bar{d}W = dU + H(M)dM \quad (1)$$

The natural variables are T and M , therefore, we write U in terms of these variables. The derivative of U with respect to M is included in the term $H(M)dM$ previously written for the work. In order not to be redundant, one of the following shall be chosen (i) $(\frac{\partial U}{\partial M})_T = 0$ and $\bar{d}W = H(M)dM$ or (ii) $\bar{d}W = 0$ and $(\frac{\partial U}{\partial M})_T = H(M)$, such that only a single contribution of the form $H(M)dM$ appears. The physical reason for (i) is as follows: if the part of the magnetic field is considered apart, the internal energy depends not on the interaction with the magnetic field, otherwise it would contradict the very idea of *internal* energy. On the second view (ii), the magnetic field would be considered a part of the system and hence, the interaction of the magnetic field with the para-magnetic substance would be present in the internal energy. With the magnetic field as part of the system there is nothing outside of the system providing work on it, and $\bar{d}W = 0$. The first approach is taken without prejudice, later we return to the second to certify our understanding of the theory is carefully taken.

$$\bar{d}Q = (\frac{\partial U}{\partial T})_M dT + H(M)dM \quad (2)$$

According to the definition of c_M ,

$$\frac{\bar{d}Q}{\partial T}|_M = c_M = c = (\frac{\partial U}{\partial T})_M \quad (3)$$

And we are able to rewrite

$$TdS = \bar{d}Q = cdT + H(M)dM \quad (4)$$

Therefore,

$$dS = \frac{c}{T}dT + \frac{H(M)}{T}dM \quad (5)$$

Notice that although $\bar{d}Q$ is not an exact differential, dS is exact. Therefore, we can integrate consistently the equations

$$(\frac{\partial S}{\partial T})_M = \frac{c}{T} \quad (6)$$

$$(\frac{\partial S}{\partial M})_T = \frac{H(M)}{T} = \frac{M}{D} \quad (7)$$

whose integration immediately provides

$$S(M, T) = c \log T + \frac{M^2}{2D} \quad (8)$$

Hence, all of the thermodynamic potentials can be determined trivially. More importantly we proceed with the second view, such that the magnetic field is included in the system. In this case, $\bar{d}W = 0$ and $(\frac{\partial U}{\partial M})_T = H(M)$,

$$\bar{d}Q = \bar{d}U = c dT + H(M) dM \quad (9)$$

In this view, dU is clearly dependent on the story, not being a state variable. One could try to cross differentiate (9) for the particular case of T and M and conclude this would not be a state function (at least not in (T, M)). However, if this is not a state function in the variables (T, M) , it is immediately not (from the equation of state and the definition of state function) a state function in any variable (for instance, in its natural variables (S, M) where one could perhaps think otherwise). The physical fact behind $\bar{d}U$ not being an exact differential can be seen to be due to the inclusion of the work of the magnetic field, which is dependent on the path.

To find the remaining potentials we start with the internal energy

$$U = TS - H(M, T)M = cT \log T + \frac{M^2 T}{2D} - \frac{M^2 T}{D} = cT \log T - \frac{M^2 T}{2D} \quad (10)$$

$$A = U - TS = -H(M, T)M = -\frac{M^2 T}{D} \quad (11)$$

$$G = A - HM = -2\frac{M^2 T}{D} \quad (12)$$

$$\mathcal{H} = U - H(M, T)M = cT \log T - \frac{3}{2} \frac{M^2 T}{2D} \quad (13)$$

One may of course write the potentials in their canonical coordinates, but this is not really done here as it produces no incremental difficult to the solution nor obliterate the physical meaning of the quantities involved.

- Answer to problem 2.3 For the blackbody radiation as the operating substance

$$P = \frac{1}{3} a T^4 \quad (14)$$

$$U = a V T^4 \quad (15)$$

$$S = \frac{4}{3} a V T^3 \quad (16)$$

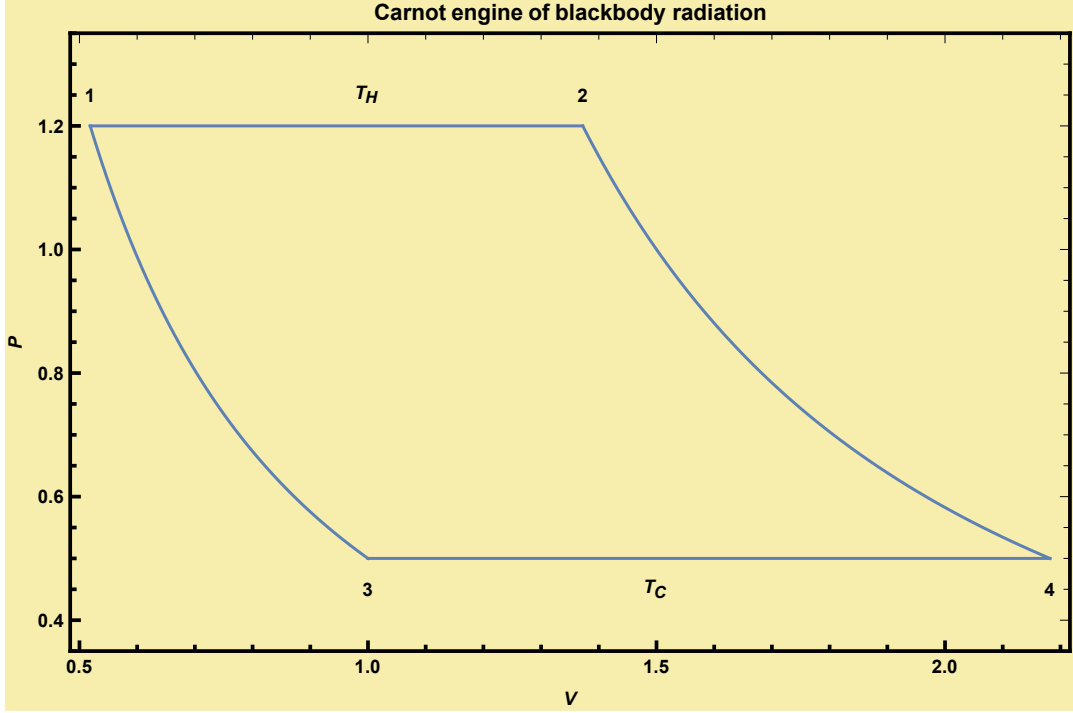
where the last has been derived in the problem 2.9. One could proceed alternatively through the fundamental equation

$$S = (U - PV)/T \quad (17)$$

As $\bar{d}Q = T dS$, in the absence of heat exchange the entropy is constant. Therefore, for the adiabatic curves

$$cte = VT^3 = V(T^4)^{3/4} \propto VP^{3/4} \quad (18)$$

The isotherms (T constant) imply P constant. Thence, the Carnot diagram can be draw.



For the second part, the total work is provided through the first law and $\Delta U = 0$ for the entire cycle.

$$\Delta U = Q - W = 0 \quad (19)$$

Implying

$$W = Q = Q_{1 \rightarrow 2} + Q_{3 \rightarrow 4} \quad (20)$$

Thence, according to the efficiency definition and the fact that the given heat to the operating system is $Q_{1 \rightarrow 2}$ (see the drawing),

$$\eta = Q = \frac{Q_{1 \rightarrow 2} + Q_{3 \rightarrow 4}}{Q_{1 \rightarrow 2}} = 1 + \frac{Q_{3 \rightarrow 4}}{Q_{1 \rightarrow 2}} \quad (21)$$

We already know $\frac{Q_{3 \rightarrow 4}}{Q_{1 \rightarrow 2}} = -\frac{T_H}{T_C}$, but we wish to verify it for the particular case of the blackbody radiation.

$$\Delta_{1 \rightarrow 2} Q = U_2 - U_1 + P(V_2 - V_1) = aV_2 T_H^4 - aV_1 T_H^4 + \frac{1}{3} a T_H^4 (V_2 - V_1) = \frac{4}{3} a T_H^4 (V_2 - V_1) \quad (22)$$

Similarly,

$$\Delta_{3 \rightarrow 4} Q = \frac{4}{3} a T_C^4 (V_4 - V_3) \quad (23)$$

Therefore,

$$\eta = 1 + \frac{T_C^4}{T_H^4} \left(\frac{V_4 - V_3}{V_2 - V_1} \right) = 1 + \frac{T_C^4}{T_H^4} \frac{V_4}{V_1} \left(\frac{1 - \frac{V_3}{V_4}}{\frac{V_2}{V_1} - 1} \right) \quad (24)$$

However, along the adiabatic we have $VT^3 = cte$, which implies the following

$$V_2 T_H^3 = V_3 T_C^3 \quad (25)$$

$$V_4 T_C^3 = V_1 T_H^3 \quad (26)$$

$$\frac{V_3}{V_4} = \frac{V_2}{V_1} \quad (27)$$

Hence,

$$\eta = 1 - \frac{T_C^4}{T_H^4} \frac{V_4}{V_1} \quad (28)$$

On the other hand,

$$\frac{V_4}{V_1} = \frac{T_H^3}{T_C^3} \quad (29)$$

which leads to

$$\eta = 1 - \frac{T_C}{T_H} \quad (30)$$

as expected.

(More on the independence of the Carnot cycle on the operating substance below)

The fact that in a Carnot cycle, regardless of the operating substance

$$\frac{Q_{3 \rightarrow 4}}{Q_{1 \rightarrow 2}} = -\frac{T_H}{T_C} \quad (31)$$

can be seen by arguments considering the entropy as a function of state. This is quite an ordinary derivation, since this is not the order in which things were first understood. The very concept of entropy was born after the above relation was canonized. However, let's proceed with a very simple proof assuming the converse order. We assume there is a function of state $dS = \frac{\bar{d}Q}{T}$. Then,

$$\frac{Q_{3 \rightarrow 4}}{Q_{1 \rightarrow 2}} = \frac{\int_{3 \rightarrow 4} T dS_{3 \rightarrow 4}}{\int_{1 \rightarrow 2} T dS_{1 \rightarrow 2}} = \frac{T_C \Delta S_{3 \rightarrow 4}}{T_H \Delta S_{1 \rightarrow 2}} \quad (32)$$

As the total variation of the entropy is null

$$\Delta S = \Delta S_{1 \rightarrow 2} + \Delta S_{2 \rightarrow 3} + \Delta S_{3 \rightarrow 4} + \Delta S_{4 \rightarrow 1} = \Delta S_{1 \rightarrow 2} + \Delta S_{3 \rightarrow 4} = 0 \quad (33)$$

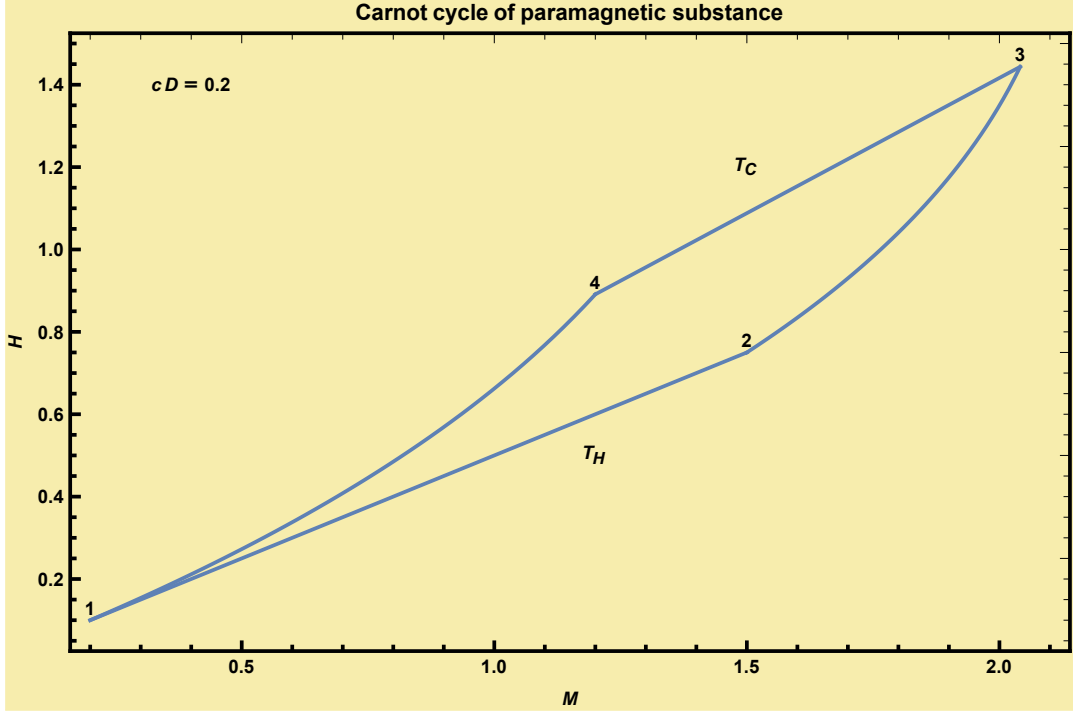
it follows the result. Naturally, along the adiabatic $\Delta S_{2 \rightarrow 3} = \Delta S_{4 \rightarrow 1} = 0$.

- Answer to problem 2.4 As we have analysed in problem 2.13,

$$\bar{d}Q = cdT + H(M)dM \quad (34)$$

Hence, for the function of state S ,

$$dS = \frac{c}{T} dT + \frac{M}{nD} dM \quad (35)$$



Thence, since S is a function of state, and consider $c = c(M, T)$,

$$\left(\frac{\partial}{\partial M}\left(\frac{c}{T}\right)\right)_T = \frac{1}{T}\left(\frac{\partial c}{\partial M}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{M}{nD}\right)\right)_M = 0 \quad (36)$$

i.e, $c = c(T)$. As $\frac{M}{H} \propto \frac{1}{T}$, along the isotherms we have straight lines departing from the origin with different inclination, higher inclination meaning lower temperature. Along the adiabatic curves $dS = 0$, and

$$\frac{c}{T}dT + \frac{M}{nD}dM = 0 \quad (37)$$

$$\frac{dMM}{nD} = -\frac{cdT}{T} \quad (38)$$

This is only possible if $M = M(T)$, therefore, we integrate to obtain the curve of interest.

$$\frac{M^2}{2D} = -c \log T = -c \log \left(\frac{nDH}{M} \right) \quad (39)$$

This is seemingly a transcendental equation for $M(H)$ with a shape similar to the W-Lambert function. Evaluating this at points 3 and 2 (and 1 and 4) produces

$$\frac{M_3^2}{2D} - \frac{M_2^2}{2D} \propto \log \frac{T_H}{T_c} \quad (40)$$

$$\frac{M_1^2}{2D} - \frac{M_4^2}{2D} \propto \log \frac{T_H}{T_c} \quad (41)$$

i.e,

$$M_1^2 - M_4^2 = -(M_3^2 - M_2^2) \quad (42)$$

To compute the heat,

$$Q_{1 \rightarrow 2} = - \int_{H_1}^{H_2} H(M) dM = \frac{T_c}{2nD} (M_1^2 - M_2^2) \quad (43)$$

$$Q_{3 \rightarrow 4} = \frac{T_H}{2nD} (M_3^2 - M_4^2) \quad (44)$$

Notice that

$$Q_{1 \rightarrow 2} / Q_{3 \rightarrow 4} = -T_C / T_H \quad (45)$$

as it should be, as $M_1^2 - M_2^2 = -(M_3^2 - M_4^2)^2$ as it can be easily obtained by rearranging $M_1^2 - M_4^2 = -(M_3^2 - M_2^2)$. Hence, the efficiency is

$$\eta = 1 - \frac{T_C}{T_H} \quad (46)$$

as expected for a Carnot engine. The total work is provided through $W = Q_{1 \rightarrow 2} + Q_{3 \rightarrow 4}$, or alternatively, $W = \eta Q_{3 \rightarrow 4}$.

- Answer to problem 2.5

From points 2 to 3 and 4 to 1 there is no work.

$$Q_{2 \rightarrow 3} = \Delta U_{2 \rightarrow 3} = \frac{3}{2} nR(T_3 - T_2) \quad (47)$$

$$Q_{4 \rightarrow 1} = \Delta U_{4 \rightarrow 1} = \frac{3}{2} nR(T_1 - T_4) \quad (48)$$

In the other paths there is no heat (adiabatic curves). Therefore, applying the first law to the whole system,

$$W = Q_{2 \rightarrow 3} + Q_{4 \rightarrow 1} \quad (49)$$

As the the positive heat given to the system is $Q_{4 \rightarrow 1}$,

$$\eta = \frac{W}{Q_{4 \rightarrow 1}} = 1 + \frac{Q_{2 \rightarrow 3}}{Q_{4 \rightarrow 1}} = 1 + \frac{T_3 - T_2}{T_1 - T_4} \quad (50)$$

The adiabatic curves can be obtained through

$$dS = \frac{dU}{T} - \frac{pdV}{T} = 0 \quad (51)$$

$$\frac{3}{2} nR \frac{dT}{T} - nR \frac{dV}{V} = 0 \quad (52)$$

which integrated produces

$$T^{3/2} V = cte \quad (53)$$

Therefore, applying this property yields

$$\frac{T_1}{T_2} = \frac{T_4}{T_3} = \left(\frac{V_2}{V_1} \right)^{2/3} \quad (54)$$

which implies

$$\frac{T_2}{T_3} = \frac{T_1}{T_4} \quad (55)$$

These relations are useful in the expression for the efficiency as one might conclude below

$$\eta = 1 + \frac{T_3(1 - \frac{T_2}{T_3})}{T_4(\frac{T_1}{T_4} - 1)} = 1 - \frac{T_3}{T_4} = 1 - (\frac{V_1}{V_2})^{2/3} \quad (56)$$

- Answer to problem 2.7

The total work is the triangle area.

$$W = \frac{J_0 L_0}{2} \quad (57)$$

Since

$$\bar{d}Q = cdT + JdL = c(\frac{\partial T}{\partial J})_L dJ + [c(\frac{\partial T}{\partial L})_J + J]dL \quad (58)$$

$$\bar{d}Q = \frac{c}{\alpha L} dJ + J(1 - \frac{c}{\alpha L^2})dL \quad (59)$$

The heat given by the system is that related to the line connecting $b \rightarrow a$, since the lines $a \rightarrow c$ and $c \rightarrow b$ corresponding to paths diminishing either J or L causes $\bar{d}Q$ to diminish as perceived through following the above expressions. We find the total heat given to the operating substance (string) either by integrating along the inclined line path, or by subtracting the total work (equal to the total heat) from the heat provided by the system during the paths $b \rightarrow c$, $c \rightarrow a$.

$$\eta = W/(W - Q_{b \rightarrow c} - Q_{a \rightarrow c}) \quad (60)$$

Integrating the heat along $J = J_0$,

$$Q_{c \rightarrow b} = -J_0(2L_0 - \frac{c}{2\alpha L_0}) = J_0 L_0(2 - \frac{c}{2\alpha L_0^2}) \quad (61)$$

Integrating the heat along $L = 2L_0$,

$$Q_{a \rightarrow c} = -(\frac{c}{2\alpha L_0^2})J_0 L_0 \quad (62)$$

Thence,

$$\eta = \frac{\frac{J_0 L_0}{2}}{[\frac{J_0 L_0}{2} + (\frac{c}{2\alpha L_0^2})J_0 L_0 + J_0 L_0(2 - \frac{c}{2\alpha L_0^2})]} = \frac{1}{3} \quad (63)$$

Another way to approach the problem is to compute directly the heat provided to the operating substance from b to a , integrating along the line with $dJ/dL = J_0/L_0$, $J = J_0 + \frac{J_0}{L_0}(L - L_0)$. Therefore,

$$\eta = \frac{J_0 L_0}{2} [\int_{L_0}^{2L_0} \frac{c}{\alpha L} \frac{J_0}{L_0} + J(1 - \frac{c}{\alpha L^2})]dL]^{-1} \quad (64)$$

- Answer to problem 2.8

$$dL = \left(\frac{\partial L}{\partial T}\right)_J dT + \left(\frac{\partial L}{\partial J}\right)_T dJ \quad (65)$$

$$dJ = \left(\frac{\partial J}{\partial L}\right)_T dL + \left(\frac{\partial J}{\partial T}\right)_L dT \quad (66)$$

Thence,

$$\left(\frac{\partial L}{\partial T}\right)_J dT + \left(\frac{\partial L}{\partial J}\right)_T \left(\frac{\partial J}{\partial L}\right)_T dL + \left(\frac{\partial L}{\partial J}\right)_T \left(\frac{\partial J}{\partial T}\right)_L dT = dL \quad (67)$$

as

$$\left(\frac{\partial L}{\partial J}\right)_T \left(\frac{\partial J}{\partial L}\right)_T = 1 \quad (68)$$

$$\left[\left(\frac{\partial L}{\partial T}\right)_J + \left(\frac{\partial L}{\partial J}\right)_T \left(\frac{\partial J}{\partial T}\right)_L\right] dT = 0 \quad (69)$$

and as

$$\left(\frac{\partial L}{\partial J}\right)_T = \left[\left(\frac{\partial J}{\partial L}\right)_T\right]^{-1} \quad (70)$$

it follows

$$\left(\frac{\partial L}{\partial T}\right)_J = -\left(\frac{\partial J}{\partial T}\right)_L / \left(\frac{\partial J}{\partial L}\right)_T \quad (71)$$

Therefore,

$$\left(\frac{\partial L}{\partial T}\right)_J = -\frac{L}{T} \left(\frac{1 - \left(\frac{L_0}{L}\right)^3}{1 + 2\left(\frac{L_0}{L}\right)^3} \right) \quad (72)$$

Thence, the thermal expansion coefficient is provided through $\lambda = -\frac{1}{T} \left(\frac{1 - \left(\frac{L_0}{L}\right)^3}{1 + 2\left(\frac{L_0}{L}\right)^3} \right)$, since $\left(\frac{\partial L}{\partial T}\right)_J = \lambda L$ defines λ . For the second item, we simultaneously find the form of the conservative field, proving the exactness by construction. Integrating

$$\left(\frac{\partial J}{\partial L}\right)_T = \frac{aT}{L_0} \left(1 + 2\left(\frac{L_0}{L}\right)^3\right) \quad (73)$$

produces

$$J = \frac{aT}{L_0} \left(L - \frac{L_0^3}{L^2}\right) = \frac{aTL}{L_0} \left(1 - \left(\frac{L_0}{L}\right)^3\right) + f(T) \quad (74)$$

Differentiating with respect to T produces

$$\left(\frac{\partial J}{\partial T}\right)_L = \frac{aL}{L_0} \left(1 + 2\left(\frac{L_0}{L}\right)^3\right) + f'(T) \quad (75)$$

which is identical to the second expression if $f(T) = cte$. For now we assume $f(T) = 0$ and we are led to

$$J = \frac{aT}{L_0} \left(L - \frac{L_0^3}{L^2}\right) \quad (76)$$

Along the adiabatic curve it is possible to write a differential equation for dS relating the size of the string at different temperatures,

$$0 = \frac{J(L, T)}{T} dL + \frac{C_L}{T} dT \quad (77)$$

which means

$$\frac{dL}{dT} = \frac{J(L, T)}{C_L} = \frac{aT}{C_L L_0} \left(L - \frac{L_0^3}{L^2} \right) \quad (78)$$

an integration produces

$$T_f = T_0 \exp \left[-\frac{a}{2C_L} \frac{L_f^2}{L_0} \left[1 + 2 \left(\frac{L_0}{L_f} \right)^3 \right] \right] \quad (79)$$

explicitly providing the relation we seek. The work is therefore simply

$$dW = J dL = C_L dT \quad (80)$$

which imply

$$W = \int C_L dT = C_L (T_f - T_0) \quad (81)$$

with T_f provided through the above expression. There is a caveat within this approach. When $L = L_0$ notice that $T \neq T_0$. But this is explained as we notice that at $L = L_0$, $J = 0$ for any given temperature T_0 (degeneracy), and therefore, the choice of the initial temperature makes it possible to keep $L = L_0$ for any choice of temperature. This degeneracy is thought to be nonphysical, and to emerge from the linear feature of the considered model.

- Answer to problem 2.9

$$dU = T dS + \mu dN - p dV \quad (82)$$

Therefore,

$$dU = T \left(\frac{\partial S}{\partial T} \right)_{NV} dT + [T \left(\frac{\partial S}{\partial N} \right)_{TV} + \mu] dN + [T \left(\frac{\partial S}{\partial V} \right)_{TN} - p] dV \quad (83)$$

Thence,

$$\left(\frac{\partial U}{\partial T} \right)_{NV} = T \left(\frac{\partial S}{\partial T} \right)_{NV} \quad (84)$$

$$\left(\frac{\partial U}{\partial V} \right)_{TN} = T \left(\frac{\partial S}{\partial V} \right)_{TN} - p \quad (85)$$

$$\left(\frac{\partial U}{\partial N} \right)_{TV} = T \left(\frac{\partial S}{\partial N} \right)_{TV} + \mu \quad (86)$$

$$(87)$$

Since

$$U = aVT^4 \quad (88)$$

$$P = \frac{1}{3} aT^4 \quad (89)$$

Then,

$$\left(\frac{\partial U}{\partial T}\right)_{NV} = 4aVT^3 = T\left(\frac{\partial S}{\partial T}\right)_{NV} \quad (90)$$

$$\left(\frac{\partial S}{\partial T}\right)_{NV} = 4aVT^2 \quad (91)$$

$$S(N, V, T) = \frac{4}{3}aVT^3 + g(N, V) \quad (92)$$

Now,

$$\left(\frac{\partial U}{\partial V}\right)_{TN} = aT^4 = T\left(\frac{\partial S}{\partial V}\right)_{TN} - p = \frac{4}{3}aT^4 + T\partial_v g - \frac{1}{3}aT^4 \quad (93)$$

Therefore,

$$\partial_v g = 0 \text{ i.e } g = g(N) \text{ but this does not produces entropy unities, therefore } g = cte \rightarrow 0 \quad (94)$$

The constant going to 0 is clearly a convention without prejudice.

In this way,

$$S(N, V, T) = \frac{4}{3}aVT^3 \quad (95)$$

As $\left(\frac{\partial U}{\partial N}\right)_{TV} = 0$,

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{TV} = 0 \quad (96)$$

- Answer to problem 2.11

$$P = \frac{Nk_B T}{V} \left[1 + \frac{N}{V} B_2(T)\right] \quad (97)$$

$$C_{V,N} = \frac{3}{2}Nk_B - \frac{N^2 k_B}{V} F(T) \quad (98)$$

In Reichl's book there is the known relation

$$\left(\frac{\partial C_{V,N}}{\partial V}\right)_{TN} = -T\left(\frac{\partial^2 P}{\partial T^2}\right)_{VN} \quad (99)$$

which allows for a shortcut, implying the necessity of

$$F(T) = -T \frac{\partial^2}{\partial T^2} [TB_2(T)] \quad (100)$$

Now we can proceed to find the entropy, once we find the Helmholtz potential

$$P = \left(\frac{\partial A}{\partial V}\right)_{TN} \quad (101)$$

Therefore,

$$A(T, V, N) = Nk_B T \log V - \frac{N^2 k_B T}{V} B_2(T) \quad (102)$$

$$S = -(\frac{\partial A(T, V, N)}{\partial T})_{VN} = -Nk_B \log V + \frac{N^2 k_B}{V} (TB_2(T))' \quad (103)$$

As

$$U = A + ST = \frac{TN^2 k_B}{V} [(TB_2(T))' - B_2(T)] = \frac{TN^2 k_B}{V} B_2'(T) \quad (104)$$

Finally, we use another relation of straightforward derivation below

$$C_{P,N} = C_{V,N} + [(\frac{\partial U}{\partial V})_{TN} - P](\frac{\partial V}{\partial T})_{P,N} \quad (105)$$

$$C_{P,N} = C_{V,N} + [-\frac{TN^2 k_B}{V^2} B_2'(T) - \frac{Nk_B T}{V} [1 + \frac{N}{V} B_2(T)]](\frac{\partial V}{\partial T})_{P,N} \quad (106)$$

And the last step is to obtain the derivative $(\frac{\partial V}{\partial T})_{P,N}$. We must solve for $V(P, T)$ the expression

$$P = \frac{Nk_B T}{V} [1 + \frac{N}{V} B_2(T)] \quad (107)$$

and apply the derivative of V with respect to T . Notice this is a second order algebraic equation, and one of the roots has to be disregarded. Indeed,

$$V = \frac{N}{\frac{k_B T}{B_2} (-1 \pm \sqrt{1 + \frac{4PB_2}{k_B^2 T^2}})} \quad (108)$$

and the positive value has to be taken.

$$V = \frac{N}{\frac{k_B T}{B_2} (-1 + \sqrt{1 + \frac{4PB_2}{k_B^2 T^2}})} = \frac{k_B T}{4P} [1 + \sqrt{1 + \frac{4PB_2(T)}{k_B^2 T^2}}] \quad (109)$$

$$(\frac{\partial V}{\partial T})_{P,N} = \frac{V}{T} + \frac{k_B T}{4P} (\frac{4P}{k_B^2}) \frac{(B_2(T)/T^2)'}{V - \frac{k_B T}{4P}} \quad (110)$$

and now we may finally have a final result with $P = P(N, V, T)$, the last relation and (97).