1 Problem 9

Superconductor phase transition.

1.1 Problem 9a

The heat capacity of a metal going to it’s super conducting state at low enough temperatures has a heat capacity

\[ C(T) = \begin{cases} C_s = V\alpha T^3 & \text{superconducting phase} \\ C_n = V [\beta T^3 + \gamma T] & \text{normal phase.} \end{cases} \]  

(1)

In general, we know that the heat capacity is

\[ C_x = \frac{dQ}{dT} \bigg|_x \]  

(2)

and when no work is being enacted on the system we have

\[ dQ = TdS. \]  

(3)

By putting these two together, we find the entropy by integrating

\[ dS \bigg|_x = \frac{C_x}{T}dT \bigg|_x \]

which for us is really:

\[ dS \bigg|_{B,\mu} = \frac{C}{T}dT \bigg|_{B,\mu} \]  

(4)

i.e. we find the entropy in the case when we had a fixed field which Kadar says is zero.

The integration results in

\[ S_s(T) - S_s(0) = \int_0^T V\alpha T^3 \frac{T}{3}dT \]

\[ = V\alpha T^3 \]

\[ S_n(T) - S_n(0) = \int_0^T V\beta T^3 + \gamma T \frac{T}{3}dT \]

\[ = V \left[ \frac{\beta}{3} T^3 + \gamma T \right] \]
By the Third Law \( \lim_{T \to 0} S = 0 \), we write these as

\[
S_s(T) = \frac{V\alpha}{3} T^3
\]  

\[
S_n(T) = V \left[ \frac{\beta}{3} T^3 + \gamma T \right]
\]

1.2 Problem 9b

When there latent heat is zero \( (L = 0) \), we are dealing with a second order transition. Since there is no latent heat there is no change in entropy. Therefore, at a critical temperature, \( T_c \), the phase change occurs and the entropies are equal

\[
S_n(T_c) = S_s(T_c)
\]

That is enough to determine what the critical temperature is

\[
S_n(T_c) = S_s(T_c)
\]

\[
\frac{V\alpha}{3} T_c^3 = V \left[ \frac{\beta}{3} T_c^3 + \gamma T_c \right]
\]

\[
\frac{1}{3} (\alpha - \beta) T_c^2 = \gamma
\]

\[
T_c^2 = \frac{3\gamma}{\alpha - \beta}
\]

\[
T_c = \pm \sqrt{\frac{3\gamma}{\alpha - \beta}}
\]

We reject the negative option as unphysical and are left with the phase transition temperature

\[
T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}}
\]

1.3 Problem 9c

So we’ve shown that when Cooper pairs are weakly coupled together the entropy does decrease due to this increased order. This of course has an effect on the energy. We assume the volume of the metal isn’t changing considerably and we still have no magnetic field so

\[
dE = TdS + \sum J_i dx_i
\]

\[
= TdS.
\]
By Eq. 1.1 we know $TdS = C_ddT$. Therefore

$$dE = CdT$$

$$\int dE_n = \int Cdt$$

$$E_n(T) - E_n(0) = \int V [\beta T^3 + \gamma T] \, dt$$

$$= V \left[ \frac{\beta T^4}{4} + \frac{\gamma T^2}{2} \right]$$

and

$$E_s(T) - E_s(0) = \frac{V \alpha T^4}{4}$$

but the question tells us

$$E(T = 0) = \begin{cases} E_n(0) = E_0 \\ E_s(0) = E_0 - V \Delta. \end{cases} \tag{10}$$

Therefore the energies are

$$E_n = V \left[ \frac{\beta T^4}{4} + \frac{\gamma T^2}{2} \right] + E_0 \tag{11}$$

$$E_s = V \left[ \frac{\alpha T^4}{4} - \Delta \right] + E_0 \tag{12}$$

### 1.4 Problem 9d

The Gibbs free energy is defined

$$G = E - TS - \sum J_i x_i. \tag{13}$$

We still say that we are in the zero field limit. There is no chemical potential difference between phases and so the Gibbs free energy at $T_c$ must be equal for both phases:

$$G_n = G_s$$

$$E_n - T_c S_n = E_s + T_c S_s$$

$$V \left[ \frac{\beta T_c^4}{4} + \frac{\gamma T_c^2}{2} \right] + E_0 - T_c V \left[ \frac{\beta}{3} T_c^3 + \gamma T_c \right] = V \left[ \frac{\alpha T_c^4}{4} - \Delta \right] + E_0 - T_c \frac{V \alpha}{3} T_c^3$$

$$\frac{\beta T_c^4}{4} + \frac{\gamma T_c^2}{2} - \frac{\beta}{3} T_c^3 - \gamma T_c^2 = \frac{\alpha T_c^4}{4} - \frac{\alpha}{3} T_c^3 - \Delta$$

$$\Delta = \frac{\gamma T_c^2}{2} + \frac{T_c^4}{4} (\alpha - \beta) - \frac{T_c^4}{3} (\alpha - \beta)$$

$$= \frac{\gamma T_c^2}{2} - \frac{T_c^4}{12} (\alpha - \beta).$$
We also know the critical temperature from Eq. 8 which we substitute in:

\[
\Delta = \frac{\gamma}{2} \frac{3\gamma}{\alpha - \beta} - \frac{\alpha - \beta}{12} \left( \frac{3\gamma}{\alpha - \beta} \right)
\]

\[
= \frac{3}{2} \frac{\gamma^2}{\alpha - \beta} - \frac{3}{4} \frac{\gamma^2}{\alpha - \beta}
\]

\[
\Delta = \frac{3}{4} \frac{\gamma^2}{\alpha - \beta}
\]

1.5 Problem 9e

We repeat the exact same Gibbs free energy balance but add a magnetic term (only to the superconduction phase)

\[
G_n = G_s
\]

\[
E_n - TS_n - 0 = E_s - TS_s + \frac{V}{8\pi} B^2
\]

16

So we know \(E_n, S_n, E_s, S_s, T_c\) and \(\Delta\) from previous questions. Sub them in (keep the temperature as \(T\) but remember when you put in \(\Delta\) that it depends on \(T_c\) not \(T\), just a warning). Then solve for \(B\).

A comment for those of you who are concerned about these sorts of things: The entropy remain unchanged (Eq. 7) as long as the heat capacity has no field dependence. The heat capacity probably does have a field dependence. But we’re assuming it’s negligble. I suppose this would always be true at “small enough” fields and so the field must be small enough that the heat capacity’s (and therefore the entropy’s) dependance on it is neglible. Furthermore, we are using the energy from Eq. 9 which must assume the field doesn’t vary. It doesn’t have to be zero but it must be constant.

Ok, back to the solution. The Gibbs free energies equal each other at the critical field - there is a different critical field for each temperature

\[
\frac{\beta T^4}{4} + \frac{\gamma T^2}{2} + E_0 - V \left[ \frac{\beta}{3} T^4 + \frac{\gamma}{2} T^2 \right] = V \left[ \frac{\alpha T^4}{4} - \Delta \right] + E_0 - \frac{V\alpha}{3} T^4 + \frac{V}{8\pi} B_c^2
\]

\[
\frac{\beta T^4}{4} + \frac{\gamma T^2}{2} - \frac{\beta}{3} T^4 - \frac{\gamma}{2} T^2 = \frac{\alpha T^4}{4} - \Delta - \frac{\alpha}{3} T^4 + \frac{B^2}{8\pi}
\]

\[
\frac{B^2}{8\pi} = \Delta + (\alpha - \beta) \frac{T^4}{12} - \frac{T^2}{12} = \frac{3}{4} \frac{\gamma^2}{\alpha - \beta} + (\alpha - \beta) \frac{T^4}{12} - \frac{T^2}{2}
\]

\[
= \left( \frac{\alpha - \beta}{12} \right) \left( T^4 - \frac{6\gamma}{\alpha - \beta} T^2 + \frac{9\gamma^2}{(\alpha - \beta)^2} \right)
\]

\[
= \left( \frac{\alpha - \beta}{12} \right) \left[ T^2 - \frac{3\gamma}{\alpha - \beta} \right]^2
\]

\[
= \left( \frac{\alpha - \beta}{12} \right) \left[ T^2 - T_c^2 \right]^2
\]
And we’re done. The order of operation inside the $(\cdot)^2$ doesn’t matter. By setting $B_0 = \sqrt{2\pi(\alpha - \beta)/3T_c} = \sqrt{2\pi\gamma}$, the critical temperature is

$$B_c = B_0 \left[1 - \left(\frac{T}{T_c}\right)^2\right]$$  \hspace{1cm} (17)

2 Problem 10

Photon gas. Don’t worry about what it is just consider the PV diagram.

2.1 Problem 10a

The work is just the area of the cycle.

$$W = dPdV.$$  \hspace{1cm} (18)

2.2 Problem 10b

The heat exchange is

$$Q = \Delta E - \Delta W$$
$$= dE + PdV|_T$$
$$= \left[\frac{\partial E}{\partial V}\right]_T dV + \left[\frac{\partial E}{\partial T}\right]_V dT + PdV|_T$$
$$= \frac{\partial E}{\partial V}|_T dV + 0 + PdV|_T$$

$$Q = \left[\frac{\partial E}{\partial V} + P\right]_T dV$$  \hspace{1cm} (19)

2.3 Problem 10c

We can express the efficiency, $\eta$, in two equivalent ways:

1. $$\eta = \frac{W}{Q}$$  \hspace{1cm} (20)

2. $$\eta = \frac{T_2 - T_1}{T_1}$$
$$= \frac{\Delta T}{T_1}$$
$$= \frac{dT}{T}$$  \hspace{1cm} (21)
By equating the two we can find

\[ \eta = \frac{dT}{T} = \frac{W}{Q} = \frac{dPdV}{\left[ \frac{\partial E}{\partial V} + P \right]_T dV} = \frac{\partial E}{\partial V}_T + P \]

Rearranging we find

\[ TdP = \left( \frac{\partial E}{\partial V}_T + P \right) dT \]  \hspace{1cm} (22)

2.4 Problem 10d

We’ve been told

\[ P = AT^4 \]  \hspace{1cm} (23)

and so we then know

\[ dP = 4AT^3dT. \]  \hspace{1cm} (24)

By substituting these two into Eq. 22, we can arrive at an expression for the energy.

\[ TdP = \left( \frac{\partial E}{\partial V}_T + P \right) dT \]

\[ T \left( 4AT^3dT \right) = \left( \frac{\partial E}{\partial V}_T + AT^4 \right) dT \]

\[ 4AT^4 = \frac{\partial E}{\partial V}_T + AT^4 \]

\[ \frac{\partial E}{\partial V}_T = 3AT^4 \]

\[ \int dE = \int 3AT^4dV \]

\[ \int dE = 3AT^4 \int dV \]

Where we remembered that we are keeping T constant and use that \( E(T = 0, V) = 0 \) to find

\[ E(T, V) = 3AVT^4 \]  \hspace{1cm} (25)
2.5 Problem 10 e

Now it’s adiabatic so $dQ = 0$ but it’s not necessarily along an idotherm. So we have

\[
dQ = 0 = dE + PdV
\]

\[
= \left. \frac{\partial E}{\partial T} \right|_V dT + \left. \frac{\partial E}{\partial V} \right|_T dV + PdV
\]

\[
= \left. \frac{\partial 3AVT^4}{\partial T} \right|_V dT + \left. \frac{\partial 3AVT^4}{\partial V} \right|_T dV + PdV
\]

\[
= 12AVT^3dT + 3AT^4dV + PdV
\]

\[
= 12AVT^3 \left( \frac{dP}{4AT^3} \right) + 3A \left( \frac{P}{A} \right) dV + PdV
\]

\[
= 3VdP + 4PdV.
\]

From here we can rearrange and integrate. Let $K$ and $K' \equiv$ the integration constants

\[
\frac{dP}{P} = \frac{-4}{3} \frac{dV}{V}
\]

\[
\ln P = \frac{-4}{3} \ln V + K
\]

\[
\ln P = \ln V^{-4/3} + K
\]

\[
P = K'V^{-4/3}
\]

\[
PV^{4/3} = \text{constant}. \tag{26}
\]

3 Problem 11 Kadar

An irreversible process between two substances at different temperatures.

3.1 Problem 11a

Show that the change of entropy must be positive.

We realize that the total change of entropy is the sum of the change of entropy in both substances:

\[
\Delta S = \Delta S_1 + \Delta S_2
\]

but the process of heat exchange is irreversible for both substances so that

\[
\Delta S_i \geq \int_{T_i}^T \frac{dQ_i}{T_i}
\]

Therefore, we must have the condition

\[
\Delta S \geq \int_{T_1}^T \frac{dQ_1}{T_1} + \int_{T_2}^T \frac{dQ_2}{T_2}. \tag{27}
\]
The heat that is received by one substance is lost by the other so we use the notation
\[ dQ = -dQ_1 = dQ_2. \]
So integrating over the temperature, the inequality reads
\[ \Delta S \geq \int_T \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = \int_T -\frac{dQ}{T_1} + \frac{dQ}{T_2} = \int_T \left( -\frac{T_2}{T_2T_1} + \frac{T_1}{T_2T_1} \right) dQ = \int_T \frac{T_1 - T_2}{T_1T_2} dQ \]
(28)

Keeping in mind our notation (Eq. 3.1), let’s consider two cases:
• \( T_1 > T_2 \): Heat flows from substance 1 to substance 2. Therefore
\[ \begin{align*}
  &\left\{ \begin{array}{l}
  dQ_2 > 0 \\
  dQ_1 < 0
\end{array} \right\} \\
  \text{but} \quad &dQ > 0 \\
  \text{therefore} \quad &T_1 - T_2 > 0 \\
  \text{therefore} \quad &\Delta S > 0
\end{align*} \]

• \( T_2 > T_1 \): Heat flows from substance 2 to substance 1. Therefore
\[ \begin{align*}
  &\left\{ \begin{array}{l}
  dQ_2 < 0 \\
  dQ_1 > 0
\end{array} \right\} \\
  \text{and} \quad &dQ < 0 \\
  \text{therefore} \quad &T_1 - T_2 < 0 \\
  \text{therefore still have} \quad &\Delta S > 0
\end{align*} \]

So for all cases, we have
\[ \Delta S \geq 0 \]  
(29)

3.2 Problem 11b

I was only able to demonstrate that the Gibbs free energy is an extrema point at equilibrium, not necessarily a minimum. We expect that it will be a minimum and never a maximum so this isn’t really a big deal.

4 Problem 4 Sethna

Blackhole has mass \( M \) (and so energy \( E = Mc^2 \)) and a radius of \( R = \frac{GM}{c^2} \).
The hole emits radiation at a temperature of
\[ T = \frac{\hbar c^3}{8\pi GMk_B} = \frac{K}{M} \]  
(30)
where we have defined \( K = \hbar c^3/8\pi Gk_B \).
4.1 Problem 4a

To calculate the specific heat that can be used (which may be negative) we use the definition of a heat capacity as already stated in Eq. 2 and the fact that no work is being done so

\[ dQ = dE - dW = dE \]

So then the heat capacity is

\[
C = \frac{\partial Q}{\partial T} = \frac{\partial E}{\partial T} = \frac{\partial M c^2}{\partial T} = \frac{\partial}{\partial T} \left( \frac{K c^2}{T} \right) = -\frac{K c^2}{T^2}
\]

\[ C = -\frac{hc^5}{8\pi Gk_B T^2} \] \hspace{1cm} (31)

OR

\[ C = -\frac{8\pi Gk_B M^2}{hc} \] \hspace{1cm} (32)
4.2 Problem 4b

To calculated the entropy of the black hole, we that \( S(M = 0) = 0 \) and that

\[
\frac{\partial S}{\partial E} = \frac{1}{T} \quad dS = \frac{dE}{T} = \frac{1}{T} \left[ Kc^2 d\left(\frac{1}{T}\right) \right] = -\frac{Kc^2}{T^3} dT
\]

\[
\int dS = -Kc^2 \int \frac{dT}{T^3}
\]

\[
S(M) - S(M = 0) = \frac{Kc^2}{2T^2}
\]

\[
S(M) - 0 = \frac{Kc^2}{2(K/M)^2}
\]

\[
S(M) = \frac{c^2 M^2}{2K} = \frac{c^2 M^2}{2 \frac{\hbar c}{8\pi Gk_B}} = \frac{4\pi Gk_B}{\hbar c} M^2
\]

\[
= \frac{4\pi Gk_B}{\hbar c} c^2 R^2
\]

\[
= A \frac{k_B c}{4\hbar G}
\]

So the entropy is directly related to the area - the rest are just universal constants.