

Homework 8 - Solutions

1st December 2004

Problem 1

(a) The difference now is that the summation goes over (n_x, n_y, n_z) and for Z_s we get

$$Z_s = \frac{e^{\epsilon_0/\tau}}{(1 - e^{-\hbar\omega/\tau})^3} \approx \frac{\tau^3 e^{\epsilon_0/\tau}}{\hbar^2 \omega^3}$$

where the last equality holds for $\tau \gg \hbar\omega$. Thus in the final answer we just need to replace the last term by $\hbar^3 \omega^3 / \tau^3$ which produces the desired answer.

(b) The enthalpy in the solid phase at high temperatures is $H_s = U + pV \approx U = -\epsilon_0 + 3\tau$. The enthalpy of the gas phase is $H_g = U + pV = \frac{3}{2}\tau + \tau = \frac{5}{2}\tau$. Their difference is the latent heat which gives $H_g - H_s = \epsilon_0 - \frac{1}{2}\tau$.

Problem 2

Since we are ignoring the entropy of solid, and its energy to the lowest order is $-N_s \epsilon_0$ the free energy of solid is $-N_s \epsilon_0$. Adding the standard formula for the free energy of the ideal gas we obtain

$$F = -N_s \epsilon_0 + N_g \tau (\log(N_g / V n_Q) - 1)$$

Writting $N_s = N - N_g$ and differentiating above with respect to N_g at constant V , N and τ we get

$$N_g = n_Q V \exp(-\epsilon_0/\tau)$$

The equilibrium vapour pressure is

$$p = - \left. \frac{\partial F}{\partial V} \right|_{\tau, N} = \frac{N_g \tau}{V} = n_Q \tau \exp(-\epsilon_0/\tau)$$

Problem 3

(a) Differentiating formula (66) on page 256 in K&K with respect to temperature gives us formula (80) in the problem:

$$\sigma_S - \sigma_N = \frac{1}{2\mu_0} \frac{dB_c^2}{d\tau}$$

As $\tau \rightarrow 0$ the $dB/dt \rightarrow 0$ - it has zero slope in the limit.

(b)

- At constant volume and particle number

$$\frac{dF_S}{dt} - \frac{dF_N}{dt} = \sigma_N - \sigma_S \rightarrow 0$$

so they merge.

- Since $U = F - \tau\sigma$ and F, τ, σ are the same for both phases at that point, the U 's are the same.

- Latent heat is the heat that we must add to go from one phase to another.

This is equal, taking $\epsilon \rightarrow 0$

$$\begin{aligned} l &= \int_{t_t-\epsilon}^{t_t+\epsilon} dQ = \int_{t_t-\epsilon}^{t_t+\epsilon} \tau d\sigma = \int_{t_t-\epsilon}^{t_t+\epsilon} \tau \frac{d\sigma}{d\tau} d\tau = \tau_t \int_{t_t-\epsilon}^{t_t+\epsilon} \frac{d\sigma}{d\tau} d\tau \\ &= \tau_t \sigma \Big|_{\tau_t-\epsilon}^{\tau_t+\epsilon} = \tau_t (\sigma_N - \sigma_S) \end{aligned}$$

where the τ_t refers to the temperature at the phase transition. At the critical point this σ 's are the same and the latent heat is 0.

(c)

$$\delta C = C_S - C_N = \tau \frac{d\sigma_S}{d\tau} + \tau \frac{d\sigma_N}{d\tau} = \frac{\tau}{2\mu_0} \frac{d^2 B_c^2}{d\tau^2}$$

We have

$$\gamma = -\frac{C_n}{\tau} = -\frac{1}{\mu_0} \left(B_c \frac{d^2 B_c}{d\tau^2} + \left(\frac{dB}{d\tau} \right)^2 \right) \rightarrow -\frac{1}{\mu_0} B_c \frac{d^2 B_c}{d\tau^2}$$

as $\tau \rightarrow 0$ because as we have shown $dB/d\tau \rightarrow 0$.

Problem 4

(a) Taking the formula for the energy at the bottom of the page 10-4 and adding the zero point energy gives

$$U = VU(0) + \frac{\pi^2 V \tau^4}{10\hbar^3 v^3}$$

From the first law

$$dU = \tau d\sigma + p dV$$

Considering process at constant V we have

$$\sigma = \int \frac{dU}{\tau} = \int 4 \frac{\pi^2 \tau^3}{10 \hbar^3 v^3} \frac{1}{\tau} d\tau = \frac{4}{3} \frac{\pi^2 \tau^3}{10 \hbar^3 v^3}$$

The free energy per unit volume is then

$$F = U - \tau \sigma = U(0) - \frac{\pi^2 \tau^4}{30 \hbar^3 v^3}$$

(b) The phase transition happens when the free energies are equal and this immediately gives the desired formula.

(c) Latent heat is the heat that we must add to go from one phase to another. This is equal, taking $\epsilon \rightarrow 0$

$$\begin{aligned} l &= \int_{t_c - \epsilon}^{t_c + \epsilon} dQ = \int_{t_c - \epsilon}^{t_c + \epsilon} \tau d\sigma = \int_{t_c - \epsilon}^{t_c + \epsilon} \tau \frac{d\sigma}{d\tau} d\tau = \tau_c \int_{t_c - \epsilon}^{t_c + \epsilon} \frac{d\sigma}{d\tau} d\tau \\ &= \tau_c \sigma \Big|_{\tau_c - \epsilon}^{\tau_c + \epsilon} = \tau_c \frac{dF}{d\tau} \Big|_{\tau_c - \epsilon}^{\tau_c + \epsilon} = \tau_c \left(\frac{dF}{d\tau} \Big|_{\beta} - \frac{dF}{d\tau} \Big|_{\alpha} \right) \\ &= \tau_c 4 \frac{\pi^2 \tau_c^3}{30 \hbar^3} (v_{\beta}^{-3} - v_{\alpha}^{-3}) = 4(U_{\beta}(0) - U_{\alpha}(0)) \end{aligned}$$

Problem 5 The curve that we are plotting is

$$p = \frac{8t/3}{V - 1/3} - \frac{3}{V^2}$$

We can do the solution for example in Mathematica. First we find where this curve has min and max by differentiating above and setting equal to zero. This gives (removing the unphysical value)

$$V_{min} = 0.7186$$

$$V_{max} = 1.5285$$

Then find the pressures at these values and this will give the pressure range where the $V(p)$ function is triple valued.

$$p_{min} = 0.4198$$

$$p_{max} = 0.7240$$

Then solve the equations $p = p_{min}$ and $p = p_{max}$ to give us the volume range where the function is triple valued. This gives

$$V_L = 0.5912$$

$$V_R = 4.6126$$

Now we would like to find a pressure of the coexistence of vapour and liquid. This happens when the $\int V dp = 0$. This pressure is such that there are three volumes $V_1 < V_2 < V_3$ at this pressure. The integral can be rewritten as $\int_{V_1}^{V_3} \frac{dp}{dV} dV$.

The procedure is for example the following. Find $\frac{dp}{dV}$ (you can also use mathematica for this). Take a pressure where the function $V(p)$ is triple valued. Find V_1 and V_3 . Integrate the above integral. This gives some value. Now vary the pressure until this values goes to zero. You can either do this by hand, or run a "For" cycle in some range, or do some fast converging algorithm that finds a zero of the function. Then you get

$$p_c \approx 0.647$$

Problem 6 Energy of one spin in a magnetic field B is $-m\mu B$ and the field produced by other spins is $B = \lambda M$ so the energy of interaction between this spin and all others is $-\lambda m\mu M$. The total interaction is obtained by summing this over all spins and dividing by two because this way we would have counted interaction of each pair of spins twice. Thus we get

$$U = -n\lambda m\mu M/2 = -\lambda M^2/2 = -n\tau_c m^2/2$$

The heat capacity per unit volume is

$$C = \frac{dU}{dT} = k_B \frac{m}{2} \frac{dm^2}{dt}$$

using

$$\frac{dm^2}{dt} = 2m \frac{dm}{dt} = \frac{1}{\cosh^2 \frac{m}{t}} \left(\frac{dm^2}{dt} \frac{1}{t} - \frac{m^2}{t^2} \right)$$

we get

$$C = n \frac{m^2}{t^2 \cosh^2 \frac{m}{t} - 1}$$

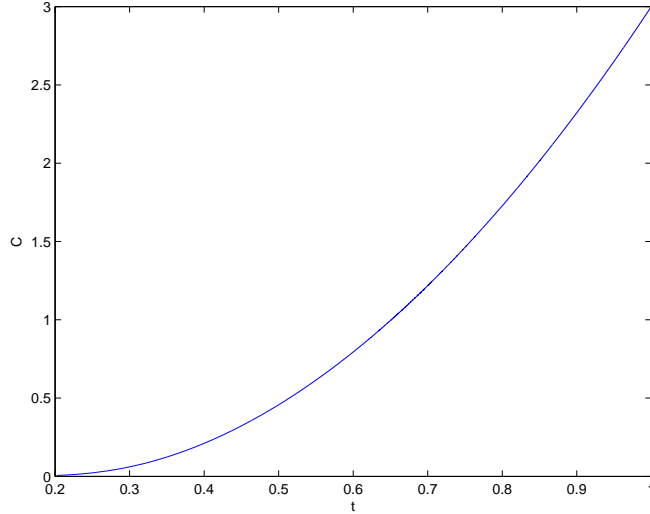


Figure 1: Heat capacity versus t .

The function is plotted on the figure (the scale of C is irrelevant).

Problem 7 (a) Metropolis algorithm: Suppose the system has available some states, each with some energy and currently is in some state. Then we want to move the system some other state. This is done as follows. Pick an available at random (each with the same probability). If it's energy is lower, accept this state. If it is higher, accept it with probability $e^{-\Delta E}$, where $\Delta E > 0$ is the difference in energies between those states.

In the case of ising spins, we have two available states. There are two ways to specialize the above algorithm to this case. First is, when we choose a state, we always choose the other state and then test it. The second is that we choose each state with the same probability and then test it.

The first way seems to be standard for the ising model and we use it in this problem.

(b)

$$p(0) = \frac{1}{1 + e^{-E/\tau}}$$

Generate x in $(0, 1)$. If $x < p(0)$ pick the zero energy state, otherwise pick the energy E state.

(c) If the vector on the right is $(1, 0)^t$ the vector on the left will be (t_{00}, t_{10}) .

Since these are the probabilities, we have $0 \leq t_{00} \leq 1$, $0 \leq t_{10} \leq 1$, $t_{00} + t_{10} = 1$. Using vector $(0, 1)^t$ we get the other three conditions.

(d) Put both vectors to be $(1, e^{-E/\tau})^t$, multiply the matrix. This gives two equations, which are identical to the desired equation using identities from the previous question.

(e) Suppose we start with the state with $E > 0$. Then metropolis algorithm for sure picks the other state. Thus $t_{01} = 1$. Now we can use above relations to fill the rest of the matrix. This gives

$$T = \begin{pmatrix} 1 - e^{-E/\tau} & 1 \\ e^{-E/\tau} & 0 \end{pmatrix}$$

However the last equation assumes that the metropolis algorithm gives canonical probabilities from canonical probabilities. Thus we should check that it indeed does.

Start with the lower energy state. Then the other state is going to be picked with probability $e^{-E/\tau}$ so $t_{10} = e^{-E/\tau}$. The other entries the follows from part (c) because that holds for general probabilities.

(f) We need to get canonical probabilities no matter what probabilities we start with. What combination of $p(0)$ and $p(E)$ doesn't depend on them? Their sum, as it is 1. Thus we will have $t_{00} = t_{01}$ and $t_{10} = t_{11}$. To get the canonical probabilities, we then need

$$T = \frac{1}{1 + e^{-E/\tau}} \begin{pmatrix} 1 & 1 \\ e^{-E/\tau} & e^{-E/\tau} \end{pmatrix}$$

Note: The problem with the metropolis algorithm mentioned - that we would always flip spin at high temperature can be avoided if we use the other version of the metropolis algorithm mentioned in part (a). In that case the matrix T would reduce to that of the canonical T .