

# 6CCP3212 Statistical Mechanics Solutions 5

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

1) This is a straightforward application of the integral formulas. Writing  $x = \beta E$ , then for the mean particle number

$$\begin{aligned} \langle N_{\text{crit}} \rangle &= \int_0^\infty \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{E^{1/2}}{e^{\beta E} - 1} dE \\ &= \int_0^\infty \frac{1}{\beta^{3/2}} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{x^{1/2}}{e^x - 1} dx \\ &= \frac{1}{\beta^{3/2}} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \Gamma(3/2) \zeta(3/2) \end{aligned} \quad (1)$$

and now using  $\Gamma(3/2) = \sqrt{\pi}/2$  and  $\zeta = 2.612$ , we get the final answer.

For the mean energy, we have a similar calculation

$$\langle E \rangle = \int_0^\infty \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{E^{3/2}}{e^{\beta E} - 1} dE \quad (2)$$

$$= \int_0^\infty \frac{1}{\beta^{5/2}} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \frac{x^{3/2}}{e^x - 1} dx \quad (3)$$

$$= \frac{1}{\beta^{5/2}} \frac{4\sqrt{2}\pi V}{(2\pi\hbar)^3} m^{3/2} \Gamma(5/2) \zeta(5/2) \quad (4)$$

and using  $\Gamma(5/2) = 3\sqrt{\pi}/4$  and  $\zeta(5/2) = 1.341$  we get the final answer.

2) (i)

$$P = \frac{Nk_bT}{V - Nb} - \frac{N^2}{V^2}a \quad (5)$$

(ii) While you can by brute force compute  $(\partial P/\partial V)_T = 0$  and  $(\partial^2 P/\partial V^2)_T = 0$ , and then solve for  $P_c$ ,  $T_c$  and  $V_c$  as functions of  $a$ ,  $b$  and  $N$ , there is a more elegant and shorter way. We first write down the Van der Waals equation of state as a polynomial in  $V$ , i.e.

$$V^3 - \left( Nb + \frac{Nk_bT}{P} \right) V^2 + \frac{aN^2}{P}V - \frac{N^3ba}{P} = 0 \quad (6)$$

But now, consider Figure 5.7 of the lecture notes – notice that for the *critical* isotherm  $T_c$ ,  $(\partial P/\partial V)_T = 0$  and  $(\partial^2 P/\partial V^2)_T = 0$  means that this at the critical point, this curve is an *inflection point* and hence has *identical roots*. Suppose  $V_c$  is this root, then the above Eq. (6) must be equivalent to  $(V - V_c)^3 = 0$ . Expanding this

$$(V - V_c)^3 = V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0. \quad (7)$$

By comparing, order by order, the coefficients of  $V^n$  between Eq. (6) and Eq. (7), we immediately get  $3V_c = Nb + Nk_bT_c/P_c$ ,  $3V_c^2 = aN^2/P_c$  and  $V_c^3 = abN^3/P_c$ . Dividing the last two equations, we get  $V_c = 3Nb$ , and then plugging this back into 2nd equation we get  $P_c = a/27b^2$ . Finally plugging both back into the  $3V_c$  equations yield the final relation  $k_bT_c = 8a/27b$ .

(iii) Using the Van der Waals equation of state, we can compute

$$\begin{aligned} \left( \frac{\partial E}{\partial V} \right)_T &= -P + T \left( \frac{\partial P}{\partial T} \right)_V \\ &= -P + \frac{Nk_bT}{V - Nb} = \frac{N^2}{V^2}a \end{aligned} \quad (8)$$

Now expressing  $E(T, V)$ , we have

$$dE = \left( \frac{\partial E}{\partial V} \right)_T dV + \left( \frac{\partial E}{\partial T} \right)_V dT \quad (9)$$

Integrating this equation over  $dV$  from some constant  $V_0$  to  $V$ , we get

$$\begin{aligned} E(T, V) &= E(T, V_0) + \int_{V_0}^V \left( \frac{\partial E}{\partial V} \right)_T dV . \\ &= E(T, V_0) + \int_{V_0}^V \frac{N^2 a}{V^2} dV \end{aligned} \quad (10)$$

We have the freedom to choose  $V_0$ . Since we are given that for the ideal gas  $C_V^{\text{id}} = (3/2)Nk_b$ , we note that the Van der Waals equation of state becomes that of the ideal gas when  $V \rightarrow \infty$ , i.e.

$$\lim_{V \rightarrow \infty} \left( \frac{Nk_b T}{V - Nb} - \frac{N^2 a}{V^2} \right) \rightarrow \frac{Nk_b T}{V} \quad (11)$$

we can choose  $V_0 \rightarrow \infty$ . The integral then becomes

$$\begin{aligned} E(T, V) &= E(T, V_0, V) + \int_{V_0}^V \frac{N^2 a}{V^2} dV \\ &= E(T, V_0 \rightarrow \infty, V) + \int_{\infty}^V \frac{N^2 a}{V^2} dV \\ &= E^{\text{id}}(T, V) - \frac{N^2 a}{V} \end{aligned} \quad (12)$$

But we are given that  $C_V^{\text{id}} = (3/2)Nk_b$ , thus  $E^{\text{id}} = (3/2)Nk_b T$ , and we get the required result

$$E = \frac{3}{2}Nk_b T - \frac{aN^2}{V} . \quad (13)$$

Since  $C_V = (\partial E / \partial T)_V$ , we have for the Van der Waals gas  $C_V = (3/2)Nk_b$ , which is independent of  $T$  and thus does not scale with  $T_c$ .

**3)** (i) The minima can be found by finding the roots of  $\partial F / \partial m = 0$ , and we get

$$2a(T - T_C)m + 2bm^3 + 2cm^5 = m(2a(T - T_C) + 2bm^2 + 2cm^4) = 0 \quad (14)$$

There are 5 solutions with the trivial solution  $m = 0$ . Setting  $z = m^2$ , we can factor the remaining terms to find a quadratic equation

$$cz^2 + bz + a(T - T_C) = 0 , \quad (15)$$

with solutions

$$z = m^2 = \frac{-b \pm \sqrt{b^2 - 4a(T - T_C)c}}{2c} \quad (16)$$

and square-root of this gives us the 4 required roots.

(ii) For  $T < T_C$ ,  $b^2 - 4a(T - T_C)c > 0$ , and  $-b + \sqrt{b^2 - 4a(T - T_C)c} > 0$  while  $-b - \sqrt{b^2 - 4a(T - T_C)c} < 0$ . Thus only 3 real roots exists. It can be easily shown that the  $m = 0$  solution is unstable (Figure 1.).

(iii) On the other hand for  $T > T_C$ , as long as the radical  $b^2 > 4a(T - T_C)c$ , there are 5 real roots. However, if  $b^2 < 4a(T - T_C)c$ , then we only have one real root at  $m = 0$ . It is easy to show that this is a stable solution (you can take derivatives of  $F$  and show that  $m = 0$  is a minima or just note that as  $m \rightarrow \pm\infty$ ,  $F \rightarrow \infty$  so the  $m = 0$  must be a minimum if it is the only root.) The point when this occur is

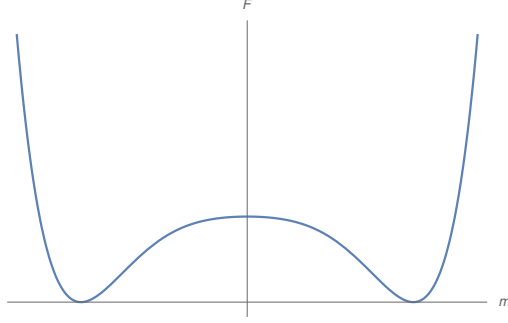


Figure 1:  $T < T_C$ .

hence  $T_* = b^2/4ac + T_C$ . Thus for  $T > T_C$ , there is a regime where  $T_C < T < T_*$  where they are 5 real roots, and with the stable solutions given by

$$m = 0, m = \pm \sqrt{\frac{-b + \sqrt{b^2 - 4a(T - T_C)c}}{2c}}. \quad (17)$$

(To see that these are the stable solutions and not

$$m = 0, m = \pm \sqrt{\frac{-b - \sqrt{b^2 - 4a(T - T_C)c}}{2c}} \quad (18)$$

(i.e. - sign in the radical), you can either by brute force calculate the derivatives, or again realize that  $F$  must look like Fig 2 and note that the maxima  $|m|$  must be smaller than the minima  $|m|$ , so we need +

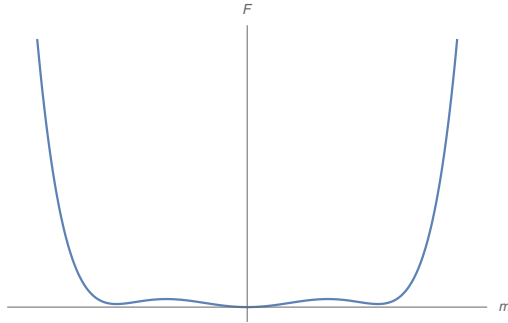


Figure 2:  $T_C < T < T_*$ .

solution for the minima.)

(iv) For question (iv) and (v), it is illustrative to plot the loci of the minima in Fig 3 Starting from  $T > T_*$  (right hand side of the figure), we are in the  $m = 0$  minima (red line). As we cool down (moving from right to left), we stay in the red line since it is the only minima. At  $T < T_*$ , there are now 3 minima (the blue lines) – however, since *we start in the red line*, the system still preferentially wants to stay in the red line as it takes energy to “go over the barrier” to the blue line. We keep cooling until we reach the end of the red line at  $T = T_C$ . As we have shown in (ii), at  $T = T_C$ , the  $m = 0$  becomes unstable, and hence the system must now “jump” to either of the blue line and undergoes a phase transition. The change in the order parameter  $m$  is, with  $T = T_C$ , is then

$$\Delta m = \sqrt{\frac{-b}{c}}. \quad (19)$$

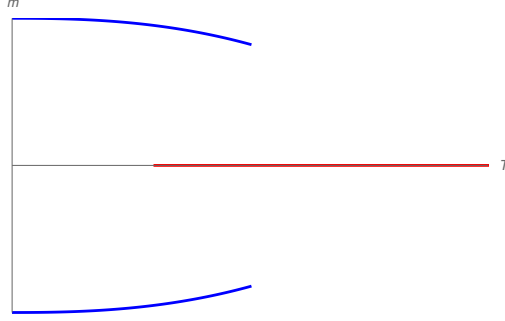


Figure 3: Loci of the minima.

(v) On the other hand, if we start with  $T < T_C$  and *heat* up the system, we begin in either of the blue lines. As we move from left to right of Fig 3, at  $T = T_C$ , the  $m = 0$  point becomes stable. However, since it is still preferentially easier to stay on the blue line, nothing happens. As the temperature reaches  $T = T_*$  however, the blue line no longer is a minima, and the system then undergoes a phase transition to the red line with  $m = 0$ . The change in the orde parameter is then

$$\Delta m = \sqrt{\frac{-b}{2c}} . \quad (20)$$

(vi) To calculate the latent heat  $L = T\Delta S$ , we need to calculate the change in the entropy  $S$  across the phase transitions. The entropy  $S$  is given by

$$S = - \left( \frac{\partial F}{\partial T} \right)_V \quad (21)$$

Since  $m$  is a function of  $T$ , there is some annoying algebra to do. A minor trick is to remember that  $F(m^2)$ , i.e. it is a function of  $m^2$ , so we can use

$$m^2(T) = \frac{-b \pm \sqrt{b^2 - 4a(T - T_C)c}}{2c} \quad (22)$$

to reduce some work. Since there are multiple minima for  $T_C < T < T_*$ , the two branches of  $S$  we need to calculate is for  $T > T_C$  and  $T < T_*$ . Along the red line,  $m = 0$ , so

$$F_{red}(m = 0) = F_0(T) \quad (23)$$

while along the blue line for  $T < T_*$ , let  $m_{\pm}$  be the two stable solutions as calculated in (iii)

$$m_{\pm} = \pm \sqrt{\frac{-b + \sqrt{b^2 - 4a(T - T_C)c}}{2c}} , \quad (24)$$

so (after a lot of algebra)

$$F_{blue}(m_{\pm}) = F_0(T) + \frac{b^3 - (b^2 - 4a(T - T_C)c)^{3/2}}{12c^2} - \frac{ab(T - T_C)}{2c} . \quad (25)$$

(There is a tricky factorization here to write it in this nice form to get the 3/2 power, but you don't have to find it since what follows don't require it.) We can then plug these into the entropy formula Eq. (21) to get

$$S_{red}(T) = - \left( \frac{\partial F_{red}}{\partial T} \right)_V \equiv S_0 \quad (26)$$

and

$$S_{blue}(T) = - \left( \frac{\partial F_{blue}}{\partial T} \right)_V = S_0 - \frac{a}{2c} \left( -b + \sqrt{b^2 - 4ac(T - T_C)c} \right) \quad (27)$$

. We can now use these to calculate the latent heat. For cooling, the transition occurs at  $T_C$ , so

$$L_{cooling} = T_C \Delta s = T_C (S_{red}(T_C) - S_{blue}(T_C)) = \frac{abT_C}{c} . \quad (28)$$

Meanwhile for heating, the transition occurs at  $T_*$  so

$$L_{heating} = T_1 \Delta s = T_C (S_{red}(T_*) - S_{blue}(T_*)) = \frac{abT_*}{2c} . \quad (29)$$

4) This question is really just for fun, since I don't expect you to solve this problem in any kind of exam. However, it is rather neat that you all have sufficient knowledge to solve a key problem in condensed matter physics – no fancy math, just 1st year math that you have forgotten and some outside the box thinking. The steps are laid out in the problem in detail. Here we will fill up the steps.

(i) The partition function is the sum over all possible energy states

$$Z = \sum_r e^{-\beta E_r} . \quad (30)$$

The form of  $E_r$  is given by the Hamiltonian

$$E = -\mu H \sum_i s_i - J \sum_{j, (n.n.)} J_{ij} s_i s_j . \quad (31)$$

We now need to count the energy states. The sum of the argument of an exponent becomes a product, i.e.  $e^{\sum_i -\beta E_i} = \prod_i e^{-\beta E_i}$  where  $i$  labels each lattice location. Meanwhile for each lattice location, each of the spin state can be  $+$  or  $-$ , thus we need to sum over them, resulting in the requested form

$$Z_{1D} = \sum_{s_i=\pm 1} \cdots \sum_{s_N=\pm 1} \prod_{i=1}^N \exp \left[ \beta J s_i s_{i+1} + \frac{\beta \mu H}{2} (s_i + s_{i+1}) \right] . \quad (32)$$

Note that at this stage, we have not made use of the fact that it is a chain (i.e.  $s_N = s_1$ .)

(ii) The four values can be easily computed by plugging the  $s_i$  in the formula, to get

$$T = \begin{pmatrix} e^{\beta J + \beta \mu H} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J - \beta \mu H} \end{pmatrix} . \quad (33)$$

(iii) This part can be a bit obtuse if you are not booked up on linear algebra. Eqn (23) in the homework problem is a direct substitution of Eqn (22) into Eqn (19), so that's easy. The tricky bit is why we can do the following “sum over all states” to get unity

$$\sum_{s_i=\pm 1} \langle s_{i-1} | T | s_i \rangle \langle s_i | T | s_{i+1} \rangle = \langle s_{i-1} | T^2 | s_{i+1} \rangle , \quad (34)$$

i.e. using the familiar formula from quantum mechanics

$$\sum_i |i\rangle \langle i| = 1 . \quad (35)$$

Assuming for now (we will prove it later) we can use this formula, then the partition function is

$$\begin{aligned} Z_{1D} &= \sum_{s_i=\pm 1} \cdots \sum_{s_N=\pm 1} \langle s_1 | T | s_2 \rangle \langle s_2 | T | s_3 \rangle \cdots \langle s_i | T | s_{i+1} \rangle \cdots \langle s_{i=N} | T | s_1 \rangle \\ &= \sum_{s_1=\pm 1} \langle s_1 | T^N | s_1 \rangle \\ &= T^N(1, 1) + T^N(-1, -1) \\ &= \text{Tr}(T^N) , \end{aligned} \quad (36)$$

which is as required. Note that we have made use of the “chain” nature of the Ising chain in line 2

Let’s now prove the formula. Consider the following term

$$\begin{aligned}
\sum_{s_2=\pm 1} \langle s_1|T|s_2\rangle\langle s_2|T|s_3\rangle &= \sum_{s_2=\pm 1} T(s_1, s_2)T(s_2, s_3) \\
&= T(s_1, +1)T(+1, s_3) + T(s_1, -1)T(-1, s_3) \\
&= \exp\left[\beta J(s_1 + s_3) + \frac{\beta\mu H}{2}(2 + s_1 + s_3)\right] + \exp\left[-\beta J(s_1 + s_3) + \frac{\beta\mu H}{2}(-2 + s_1 + s_3)\right] \\
&\equiv A(s_1, s_3)
\end{aligned} \tag{37}$$

where we have defined the new operator. Now this operator has the following matrix form

$$A = \begin{pmatrix} e^{-2\beta J+2\beta(\mu H+J)} & e^{-\beta\mu H} + e^{\beta\mu H} \\ e^{-\beta\mu H} + e^{\beta\mu H} & e^{-2\beta J+2\beta(\mu H+J)} \end{pmatrix} \tag{38}$$

and hence we can write the operator  $A$  as

$$\langle s_1|A|s_3\rangle = A(s_1, s_3) . \tag{39}$$

For Eq. (34) to be true, this must be equal to

$$\langle s_1|A|s_3\rangle = \langle s_1|T^2|s_3\rangle \tag{40}$$

where  $T$  is the transfer matrix Eq. (33). But it is easy to show that via some algebra

$$T^2 = A , \tag{41}$$

and our proof is complete.

(v) The eigenvalue of  $T$  are easily computed using the standard formula for  $2 \times 2$  matrix, so I will not show them here. Again from standard linear algebra formula for any non-degenerate square matrix  $A$ ,  $\text{Tr}(A^N) = \sum_i \lambda_i^N$  where  $\lambda_i$  are the eigenvalues of the  $A$ , we get the final answer.