

PHYSICS 112
Homework 9 Solutions

1. As discussed in class the (Helmholtz) free energy of the van der Waals gas is given by

$$F = -Nk_B T \left\{ \ln \left[\frac{n_Q(V - Nb)}{N} \right] + 1 \right\} - N \frac{N}{V} a,$$

where

$$n_Q = \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}.$$

- (a) The entropy is given by

$$\begin{aligned} S &= - \left(\frac{\partial F}{\partial T} \right)_{V,N} \\ &= Nk_B \left\{ \ln \left[\frac{n_Q(V - Nb)}{N} \right] + 1 \right\} + Nk_B T \frac{\partial \ln T^{3/2}}{\partial T} \\ &= \boxed{Nk_B \left\{ \ln \left[\frac{n_Q(V - Nb)}{N} \right] + \frac{5}{2} \right\}}. \end{aligned}$$

- (b) The energy can be obtained either from $U = F + TS$ or $U = (\partial/\partial\beta)(\beta F)$. Since we have already worked out the entropy the simplest is to use $U = F + TS$ which gives

$$\boxed{U = N \left[\frac{3}{2} k_B T - \frac{N}{V} a \right]}.$$

The first term is the usual kinetic energy, and the second term is the (negative) potential energy from the attractive part of the potential. There is no contribution from the strong repulsive part of the potential, (which involves the parameter b in the van der Waals equation) because it acts like to hard wall from which the particles simply recoil.

2. (a) In the model in the book we have a solid in equilibrium with a vapor. For the vapor the “activity” $\lambda_g \equiv \exp(\beta\mu_g)$ is given by

$$\lambda_g = nV_Q = \frac{P}{k_B T} V_Q = \frac{P}{k_B T} \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2}.$$

For the solid the Gibbs free energy per atom, g_s , is related to the chemical potential by $g_s = f_s + Pv_s = \mu_s$, where f_s is the Helmholtz free energy per atom. The pressure in the solid is the same as that in the gas but the volume per atom v_s is much less than that in the gas, so we neglect the Pv_s term. Hence the activity in the solid is given by

$$\lambda_s \equiv \exp(\beta\mu_s) \simeq \exp(\beta f_s) = \exp(-\ln Z_s) = \frac{1}{Z_s},$$

where Z_s is the partition function of an atom in the solid.

We represent the solid by a three-dimensional harmonic oscillator. The energy levels are $E = -\epsilon_0 + \hbar\omega(n_x + n_y + n_z)$, where n_x, n_y and n_z are positive integers or zero. Hence we have

$$Z_s = \sum_{n_x, n_y, n_z} \exp \{ -\beta[(n_x + n_y + n_z)\hbar\omega - \epsilon_0] \} = \exp(\beta\epsilon_0) \left[\sum_n \exp(-n\beta\hbar\omega) \right]^3 = \frac{\exp(\beta\epsilon_0)}{[1 - \exp(\beta\hbar\omega)]^3}.$$

We consider high temperatures where $k_B T \gg \hbar \omega$ and so get

$$\lambda_s \simeq \frac{1}{Z_s} \simeq \left(\frac{\hbar \omega}{k_B T} \right)^3 \exp(-\beta \epsilon_0).$$

Equilibrium occurs when $\lambda_s = \lambda_g$ which gives

$$\frac{P}{k_B T} \left(\frac{2\pi \hbar^2}{m k_B T} \right)^{3/2} \simeq \left(\frac{\hbar \omega}{k_B T} \right)^3 \exp(-\beta \epsilon_0),$$

which simplifies to

$$\boxed{P \simeq \left(\frac{m}{2\pi} \right)^{3/2} \frac{\omega^3}{(k_B T)^{1/2}} \exp(-\beta \epsilon_0)}. \quad (1)$$

(b) According to Eq. (18) of Ch. 10 of the book

$$\frac{dP}{dT} \simeq \frac{L}{k_B T^2} P,$$

where L is the latent heat per atom. Substituting P from Eq. (1) gives

$$\frac{\epsilon_0 - k_B T/2}{k_B T^2} = \frac{L}{k_B T^2}$$

and so the latent heat per atom L is given by

$$\boxed{L = \epsilon_0 - \frac{k_B T}{2}}.$$

(c) A phenomenological explanation of this last result is as follows. As discussed in the book the latent heat is also the change in the enthalpy, see KK p. 284-5. The enthalpy of the vapor phase is related to the specific heat at constant pressure by $C_p = (\partial H / \partial T)_p$. We showed in class that C_p of an ideal gas is $(5/2)Nk_B$, and so the enthalpy of the vapor phase is

$$H_g = \frac{5}{2} k_B T$$

per particle.

For the solid, the binding energy is $-\epsilon_0$ and the excitation energy of the oscillators is, on average, $k_B T$ for each of the x , y , and z , directions. Hence the mean energy is $U_s = -\epsilon_0 + 3k_B T$ per particle. Now $H = U + PV$ but the volume is small for the solid (as also used above) so $H_s \simeq U_s$ and we have

$$H_s = -\epsilon_0 + 3k_B T$$

per particle. The latent heat is therefore

$$L = H_g - H_s = \frac{5}{2} k_B T - (-\epsilon_0 + 3k_B T) = \boxed{\epsilon_0 - \frac{1}{2} k_B T},$$

as found explicitly above,

3. (a) The energy is given by $E = -\gamma B \cos \theta$, where θ is the polar angle of the spins, which we take to be along the direction of the magnetic field. Remembering that in spherical polars the angular integrals are of the form $\int \sin \theta d\theta d\phi$, and noting that there is no dependence of ϕ , we have

$$m \equiv \gamma \langle \cos \theta \rangle = \frac{\int_0^\pi e^{t \cos \theta} \cos \theta \sin \theta d\theta}{\int_0^\pi e^{t \cos \theta} \sin \theta d\theta} = \frac{\int_{-1}^1 e^{tx} x dx}{\int_{-1}^1 e^{tx} dx},$$

where $t = \beta \gamma B$ and $x = \cos \theta$. The denominator is $\sinh(t)/t$ and the numerator is d/dt of the numerator = $\cosh(t)/t - \sinh(t)/t^2$. Hence

$$m = \gamma L(\beta \gamma B),$$

where

$$L(x) = \coth(x) - \frac{1}{x}.$$

Note: $L(x)$ is called the Langevin function. For small x it has the series expansion $L(x) = x/3 - x^2/45 + \dots$, and for $x \rightarrow \infty$, $L(x) \rightarrow 1$.

- (b) No. The energy is invariant if the spin and field are both rotated by the same amount. Only the field gives a preferred direction in space, and so the spin always points along the direction of the field. If the direction of the field is changed, by symmetry, the spin will point along the *new* direction of the field, and the magnitude of the spin expectation value will not change.

4. From the thermodynamic identity $dF = SdT - MdB$ we have

$$S = - \left(\frac{\partial F}{\partial T} \right)_B, \quad M = - \left(\frac{\partial F}{\partial B} \right)_T.$$

Since the order of the mixed second derivatives of F is unimportant we have the Maxwell relation

$$\left(\frac{\partial M}{\partial T} \right)_B = \left(\frac{\partial S}{\partial B} \right)_T.$$

According to the third law of thermodynamics $S = 0$ at $T = 0$, and so $(\partial S/\partial B)_T = 0$ at $T = 0$. According to the above Maxwell equation, this implies

$$\left(\frac{\partial M}{\partial T} \right)_B = 0,$$

at $T = 0$.

5. The web site is <http://physics.ucsc.edu/~peter/ising/ising.html>.

- (a) The range of the correlations is quite small. The system quickly settles down to a state which (statistically) doesn't depend on the starting state.
- (b) The correlated regions are now large. The fluctuations of these large correlated regions are quite slow.

- (c) The state is ordered, with virtually all spins down (white) and just a few flipped spins. With a random start, domains of both signs grow, and usually, for some time, there is one large white domain and one large blue domain. Eventually one of these will grow at the expense of the other, and we will have a ordered state with just a few overturned spins, as when when we started with an ordered state. This is an example of “spontaneous symmetry breaking”.

6. (a) Consider

$$m = \tanh\left(\frac{J_0 m + B}{k_B T}\right), \quad (2)$$

for $T > T_c = J_0/k_B$ and $B \rightarrow 0$. In this limit $m \rightarrow 0$ as shown in class. Hence we will differentiate this expression with respect to B (remembering that *both* factors of m must be differentiated) and then set $m = B = 0$. The differentiation gives (with $\chi \equiv \partial m/\partial B$)

$$\chi = \frac{J_0 \chi + 1}{k_B T} \operatorname{sech}^2\left(\frac{J_0 m + B}{k_B T}\right),$$

Setting $m = B = 0$ the sech becomes unity, and so

$$\chi = \frac{J_0 \chi + 1}{k_B T},$$

which can easily be arranged to

$$\chi = \frac{1}{k_B(T - T_c)}.$$

Note: This shows that the system is very sensitive to a small magnetic field just above the transition temperature. This should not be surprising because below T_c the magnetization appears *spontaneously* without any applied field at all.

- (b) Going back to Eq. (2) and setting $T = J_0/k_B (= T_c)$, and using $\tanh(x) = x - x^3/3 + \dots$ gives

$$m = (m + b) - \frac{1}{3}(m + b)^3 + \dots,$$

where $b = B/k_B T$. This immediately gives

$$(m + b)^3 = 3b. \quad (3)$$

For $b \rightarrow 0$ the solution is $m \sim b^{1/3}$ so $m \gg b$ and the factor of b on the LHS of Eq. (3) can be neglected compared with m . Hence we get

$$m \sim b^{1/3} \boxed{\sim B^{1/3}}.$$

7. As discussed in class the mean field H is given, in the absence of an external field, by

$$H = zJ\langle S \rangle = zJm$$

where $m = \langle S \rangle$ is the magnetization. In a field H the energy states of a spin are, for the spin-1 case,

$$\begin{aligned} S = 1, & \quad E = -H \\ S = 0, & \quad E = 0 \\ S = -1, & \quad E = H \end{aligned}$$

Hence the expectation of S is given by

$$m = \frac{e^{\beta H} + 0 - e^{-\beta H}}{e^{\beta H} + 1 + e^{-\beta H}},$$

or

$$m = \frac{2 \sinh\left(\frac{zJm}{k_B T}\right)}{1 + 2 \cosh\left(\frac{zJm}{k_B T}\right)}.$$

To get the temperature of the transition, assumed second order, expand the RHS to first order in m , i.e.

$$m = \frac{2zJ}{3k_B T} m + \dots$$

The transition is where the coefficients of m on both sides of the equation are equal, i.e.

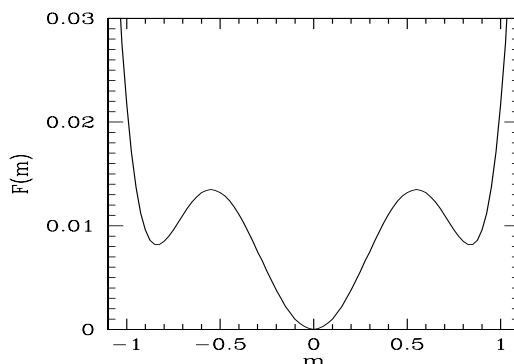
$$\boxed{k_B T_c = \frac{2}{3} zJ.}$$

8. We consider the Landau free energy

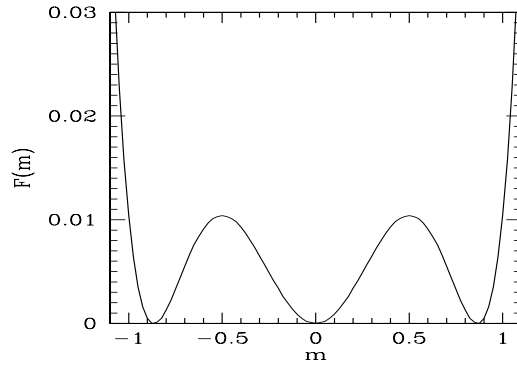
$$F(m) = \frac{1}{2} a(T) m^2 + \frac{1}{4} c m^4 + \frac{1}{6} d m^6.$$

We discussed in class the case of $c > 0$, and showed that the equilibrium value of m tends to zero *continuously*. If $c < 0$ then, while $a(T)$ is small but positive, $F(m)$ initially decreases as m increases from 0 (because $(a(T)m^2)$ dominates), then $F(m)$ starts to decrease (because $c m^4$ dominates in this region), and then finally, for large m , $F(m)$ increases because $d m^6$ dominates. Hence $F(m)$ starts to develop minima at non-zero m even above T_0 (i.e. where $a(T) > 0$), as shown in the figures below.

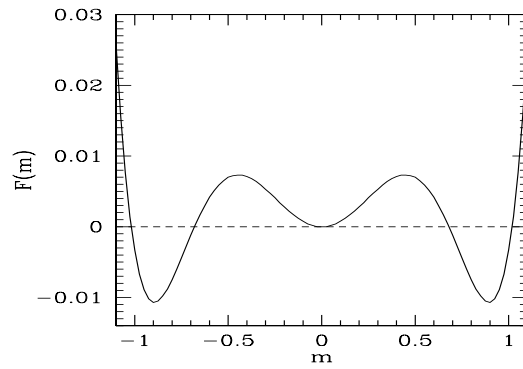
One can also locate, mathematically, where the first order transition occurs by determining m^* and T as a function of $a(T) (\equiv \alpha(T - T_0))$, b , c and d , such that $\partial F / \partial m|_{m^*} = 0$, and $F(m^*) = F(0) (= 0)$.



At $T = T_c$ the free energy of these two (equivalent) minima is equal to that of the $m = 0$ solution. See the figure below.



For $T < T_c$ the solutions at non-zero m have the lowest free energy, as shown in the figure below.



Let $\pm m_0$ be the value of m at the two minima at non-zero m in middle of the three figures above. The figures show that the magnetization drops discontinuously from m_0 to 0 at T_c . In other words the transition is discontinuous if $c < 0$.