Assignment 7

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1 Kardar Ch. 5 Problem 10

Consider binary alloy with N_A atoms of types A and N_B atoms of type B. There is an attractive enery of $-J$ between like neighbours but a repulsive energy of $+J$ between dissimilar neighbours. Imagine the atoms are on a cubic lattice (6 nearest neighbours).

1.1 Part a)

Since the particles are attracted to similar atoms and repulsed by dissimilar ones when the mixing effects of thermal noise go to zero the alloy will phase separate into pure A and pure B phases.

1.2 Part b)

In the other extreme (very hot) the particles will be randomly distributed on the $N = N_A + N_B$ sites *i.e.* the probability of finding an A-type atom at some site is $p_A = N_A/N$, *etc.* In this case, the energy is the number of bonds (6/2 for each site) times the average energy of each bond. The average attractive energy is $-Jp_A^2 - Jp_B^2$ and the average repulsive energy is Jp_Ap_B so then the average energy of the system is

$$\begin{aligned} E &= 3N\left(-Jp_A^2 - Jp_B^2 + Jp_Ap_B\right) \\ &= 3NJ\left(p_Ap_B - p_A^2 - p_B^2\right) \end{aligned}$$

$$\boxed{E = -3NJ\left(p_A - p_B\right)^2}. \tag{1}$$

1.3 Part c)

In the same limit of a very hot alloy the entropy of mixing N_A and N_B atoms is

$$\boxed{S = k_{\mathrm{B}} \ln\left(\frac{N!}{N_A!N_B!}\right)}. \tag{2}$$

Assuming a large number of both types, we can take Sterling's approximation of each term

$$\begin{aligned} S &= k_{\mathrm{B}} \left(\ln N! - \ln N_A! - \ln N_B!\right) \\ &\approx k_{\mathrm{B}} \left(N \ln N - N_A \ln N_A - N_B \ln N_B\right) \\ &= k_{\mathrm{B}} N \left(\ln N - p_A \ln N_A - p_B \ln N_B\right) \end{aligned}$$

$$\boxed{S = -k_{\mathrm{B}} N \left(p_A \ln p_A + p_B \ln p_B\right)}. \tag{3}$$

1.4 Part d)

From the above to section, we can give the free energy as a function of $x = \left(N_A - N_N\right)/N = p_A - p_B$ to be

$$\begin{aligned} F &= E - TS \\ &\approx -3NJ \left(p_A - p_B\right)^2 + k_{\mathrm{B}} T N \left(p_A \ln p_A + p_B \ln p_B\right) \\ &= -3NJx^2 + N k_{\mathrm{B}} T \left[\left(\frac{1+x}{2}\right) \ln\left(\frac{1+x}{2}\right) + \left(\frac{1-x}{2}\right) \ln\left(\frac{1-x}{2}\right)\right] \end{aligned}$$

which we expand to 4^{th} order to get

$$F \approx -3NJx^2 - N k_{\mathrm{B}} T \ln 2 + N \frac{k_{\mathrm{B}} T}{2} x^2 + \frac{N k_{\mathrm{B}} T}{12} x^4 + \ldots$$

$$\boxed{F = -N k_{\mathrm{B}} T \ln 2 + \left(N \frac{k_{\mathrm{B}} T}{2} - 3JN\right) x^2 + \frac{N k_{\mathrm{B}} T}{12} x^4}. \tag{4}$$

To look at the convexity of F, we take the second derivative:

$$\frac{\partial^2 F}{\partial x^2} = 2 \left(N \frac{k_{\mathrm{B}} T}{2} - 3JN\right) + N k_{\mathrm{B}} T x^2 \tag{5}$$

At small x this critical temperature T_c where F'' becomes zero is

$$\boxed{k_{\mathrm{B}} T_c = 6J}. \tag{6}$$

1.5 Part e)

The function is concave for

$$\frac{\partial^2 F}{\partial x^2} < 0$$

which requires from Eq. 5 that

$$\begin{aligned} 0 &> 2 \left(N \frac{k_{\mathrm{B}} T}{2} - 3JN\right) + N k_{\mathrm{B}} T x^2 \\ x^2 &< \frac{2}{N k_{\mathrm{B}} T} \left(3JN - N \frac{k_{\mathrm{B}} T}{2}\right) \\ &< \left(\frac{6J}{k_{\mathrm{B}} T} - 1\right) \\ &< \left(\frac{T_c}{T} - 1\right) \end{aligned}$$

The boarder of this region is when

$$\boxed{x = x_{sp} = \sqrt{\frac{T_c}{T} - 1}}. \tag{7}$$

1.6 Part f)

The line between A-rich and B-rich (called X_{eq}) occurs for minimized free energy. So then we solve for x_{eq}:

$$\begin{aligned}\frac{\partial F}{\partial x}(x = x_{eq}) = 0 & \\ &= (Nk_{\mathrm{B}}T - 6JN)\, x_{eq} + \frac{Nk_{\mathrm{B}}T}{3} x_{eq}^3 \\ &= 1 - 6\frac{J}{k_{\mathrm{B}}T} + \frac{x_{eq}^2}{3}\end{aligned}$$

$$\boxed{x_{eq} = \pm\sqrt{18\frac{J}{k_{\mathrm{B}}T} - 3}} \tag{8}$$

which only applies when $T < T_c$ since if $T > T_c$ it's homogenous mixture and no phase separating will occur.

2 Kardar Ch. 7 Problem 11

Consider Bose condensation in d-D of non-interaction bosons in a volume of L^d.

2.1 Part a.i)

We know that from the text that the grand partition function is

$$\mathcal{Q}_\eta = \sum_{\{n_{\vec{k}}\}}^{\eta} \prod_{\vec{k}} \exp\left[-\beta\,(\epsilon - \mu)\, n_{\vec{k}}\right]$$

which for bosons takes $\eta = +1$ and $n_{\vec{k}} = 0, 1, 2, \ldots$ such that

$$\mathcal{Q}_+ = \prod_k \left[1 - \exp\left(\beta\mu - \beta\epsilon(k)\right)\right]^{-1}. \tag{9}$$

This mean that the grand potential is

$$\mathcal{G} = -k_{\mathrm{B}}T \ln \mathcal{Q} = -k_{\mathrm{B}}T \sum_k \ln\left(\frac{1}{1 - \exp\left(\beta\mu - \beta\epsilon(k)\right)}\right). \tag{10}$$

If we go to the continuum limit, then we should replace the sum with d-D integration:

$$\begin{aligned}
\mathcal{G} &= k_{\mathrm{B}}T\sum_{k}\ln\left(1-\exp\left(\beta\mu-\beta\epsilon(k)\right)\right)\\
&= k_{\mathrm{B}}T\int\frac{V}{\left(2\pi\right)^{d}}d^{d}k\ln\left(1-\exp\left(\beta\mu-\beta\epsilon(k)\right)\right)\\
&= k_{\mathrm{B}}T\frac{V}{\left(2\pi\right)^{d}}S_{d}\int k^{d-1}dk\ln\left(1-z\exp\left(-\beta\epsilon(k)\right)\right)
\end{aligned}$$

where $S_d = 2\pi^{d/2}/\left(d/2-1\right)!$ and $z = e^{\beta\mu}$. We replace $\epsilon = \hbar^2 k^2/2m$ since we're talking about photons but then to do the integral make the variable change:

$$\begin{aligned}
x &= \frac{\beta\hbar^{2}k^{2}}{2m}\\
k &= \sqrt{\frac{2mx}{\beta\hbar^{2}}}\\
dk &= dx\sqrt{\frac{2m}{\beta x}}\frac{1}{2\hbar}
\end{aligned}$$

which leads to the grand potential

$$\begin{aligned}
\mathcal{G} &= k_{\mathrm{B}}T\frac{V}{\left(2\pi\right)^{d}}S_{d}\int k^{d-1}dk\ln\left(1-z\exp\left(-\beta\epsilon(k)\right)\right)\\
&= k_{\mathrm{B}}T\frac{V}{\left(2\pi\right)^{d}}S_{d}\int\left(\frac{2mx}{\beta\hbar^{2}}\right)^{\frac{d-1}{2}}dx\left(\frac{2m}{\beta x}\right)^{1/2}\frac{1}{2\hbar}\ln\left(1-ze^{-x}\right)\\
&= k_{\mathrm{B}}T\frac{V}{\left(2\pi\right)^{d}}S_{d}\frac{\left(2m\right)^{d/2}}{2\hbar^{d}\beta^{d/2}}\int x^{d/2-1}\ln\left(1-ze^{-x}\right)dx\\
&= k_{\mathrm{B}}T\frac{VS_{d}}{2}\left(\frac{m}{\pi^{2}\hbar^{2}\beta}\right)^{d/2}\int x^{d/2-1}\ln\left(1-ze^{-x}\right)dx.
\end{aligned}$$

This is where we will use the integration by parts (as hinted by the question). Let

$$\begin{aligned}
dv &= x^{d/2-1}dx\\
u &= \ln\left(1-ze^{-x}\right)\\
v &= \frac{2}{d}x^{d/2}\\
du &= -\frac{z}{1-ze^{-x}}dx
\end{aligned}$$

such that

$$
\begin{aligned}
\mathcal{G} &= k_{\mathrm{B}}T\frac{VS_d}{2}\left(\frac{m}{\pi^2\hbar^2\beta}\right)^{d/2}\left[uv|_0^\infty - \int vdu\right] \\
&= k_{\mathrm{B}}T\frac{VS_d}{2}\left(\frac{m}{\pi^2\hbar^2\beta}\right)^{d/2}\left[0 - \int \frac{2}{d}x^{d/2}\frac{z}{1-ze^{-x}}dx\right] \\
&= -k_{\mathrm{B}}T\frac{VS_d}{d}\left(\frac{m}{\pi^2\hbar^2\beta}\right)^{d/2}\int \frac{x^{d/2}}{z^{-1}e^x-1}dx \\
&= -k_{\mathrm{B}}T\frac{VS_d}{d}\left(\frac{m}{\pi^2\hbar^2\beta}\right)^{d/2}\Gamma\left(\frac{d}{2}+1\right)f^+_{\frac{d}{2}+1}(z).
\end{aligned}
$$

If you remember $\Gamma(x+1) = x\Gamma(x)$ and $\Gamma(n/2) = (2\pi)^{n/2}$ when $n \in I$ you can simplify this a bit to

$$
\boxed{\mathcal{G} = -k_{\mathrm{B}}T\frac{VS_d}{2}\left(\frac{m}{\pi^2\hbar^2\beta}\right)^{d/2}(2\pi)^{d/2}f^+_{\frac{d}{2}+1}(z)}. \tag{11}
$$

or if you like using λ this is

$$
\boxed{\mathcal{G} = -k_{\mathrm{B}}T\frac{V}{\lambda^d}f^+_{\frac{d}{2}+1}(z)}. \tag{12}
$$

2.2 Part a.ii)

From the grand partition function we can find the average number of particles to be

$$
\begin{aligned}
N &= -\frac{\partial\mathcal{G}}{\partial\mu} \\
&= k_{\mathrm{B}}T\frac{V}{\lambda^d}\frac{\partial}{\partial\mu}f^+_{\frac{d}{2}+1}(z)
\end{aligned}
$$

The textbook showed that the derivative is recursive (see page 194 which shows $df^+_m/dz = f^+_{m-1}/z$) so

$$
\begin{aligned}
N &= k_{\mathrm{B}}T\frac{V}{\lambda^d}\frac{\partial}{\partial\mu}f^+_{\frac{d}{2}+1}(z) \\
&= k_{\mathrm{B}}T\frac{V}{\lambda^d}\left(\frac{\partial z}{\partial\mu}\right)\frac{\partial}{\partial z}f^+_{\frac{d}{2}+1}(z) \\
&= k_{\mathrm{B}}T\frac{V}{\lambda^d}\beta f^+_{\frac{d}{2}}(z).
\end{aligned}
$$

which means that the average density n is

$$
\boxed{n = \frac{N}{V} = \frac{f^+_{\frac{d}{2}}(z)}{\lambda^d}}. \tag{13}
$$

2.3 Part b)

To find PV/E recall that

$$PV = -\mathcal{G} \tag{14}$$

and

$$E = \beta \frac{\partial \mathcal{G}}{\partial \beta} \tag{15}$$

from Chapter 4. So then the energy is

$$\begin{aligned} E &= \beta \frac{\partial \mathcal{G}}{\partial \beta} \\ &= -V f^{+}_{\frac{d}{2}+1}\left(z\right) \frac{\partial}{\partial \beta} \frac{1}{\lambda^d} \\ &= -V f^{+}_{\frac{d}{2}+1}\left(z\right) \frac{\partial}{\partial \beta} \left(\frac{2\pi m}{h^2 \beta}\right)^{d/2} \\ &= \frac{d}{2\beta} V f^{+}_{\frac{d}{2}+1}\left(z\right) \left(\frac{2\pi m}{h^2 \beta}\right)^{d/2} \end{aligned}$$

$$\boxed{E = -\frac{d}{2}\mathcal{G}} \tag{16}$$

and now it's trivial to see

$$\boxed{\frac{PV}{E} = \frac{2}{d}}. \tag{17}$$

2.4 Part c)

To find the critical temperature, we can repeat the textbook's derivation for d-D or just extrapolate from Kardar's 3-D solution:

$$T_c\left(n\right) = \frac{h^2}{2\pi m k_{\mathrm{B}}} \left(\frac{n}{g \zeta_{3/2}}\right)^{2/3}$$

by replacing every 3 with a d and setting $g = 1$ for photons to get

$$\boxed{T_c\left(n\right) = \frac{h^2}{2\pi m k_{\mathrm{B}}} \left(\frac{n}{\zeta_{d/2}}\right)^{2/d}} \tag{18}$$

2.5 Part d)

Finding the heat capacity is easy since we already found E

$$\begin{aligned} C &= \frac{\partial E}{\partial T} \\ &= -\frac{d}{2} \frac{\partial \mathcal{G}}{\partial T}. \end{aligned}$$

The derivative is just like the one we did to find E in the first place so

$$\begin{aligned}
C &= -\frac{d}{2}\frac{\partial \mathcal{G}}{\partial T} \\
&= \frac{d}{2}\left(-\left[\frac{d}{2}+1\right]\right)\frac{\mathcal{G}}{T} \\
&= -\frac{d}{2}\left(\frac{d}{2}+1\right)\frac{\mathcal{G}}{T}.
\end{aligned}$$

We interpret $T < T_c$ to mean $z \to 1$ which means

$$\begin{aligned}
\lim_{z\to 1} C(T) &= -\frac{d}{2}\left(\frac{d}{2}+1\right)\lim_{z\to 1}\frac{\mathcal{G}}{T} \\
&\approx \frac{d}{2}\left(\frac{d}{2}+1\right)\frac{1}{T}k_{\mathrm{B}}T\frac{V}{\lambda^d}f^{+}_{\frac{d}{2}+1}(1)
\end{aligned}$$

$$\boxed{C \approx \frac{d}{2}\left(\frac{d}{2}+1\right)\frac{Vk_{\mathrm{B}}}{\lambda^d}\zeta_{\frac{d}{2}+1}}. \tag{19}$$

3 Kardar Ch. 7 Problem 17

We want to talk about the electrons in graphene. So they are relativistic 2-D fermions of spin 1/2 giving $g = 2$ and an energy of

$$\epsilon_{\pm}(\vec{k}) = \pm\hbar v\left|\vec{k}\right| \tag{20}$$

3.1 Part a)

At $T = 0$ all the negative energy states are occupied and all the positive states are empty. So we can imagine the system to be made up of two *phases*. Electrons in the negative state and holes in the positive state. At $T = 0$ the two phases coexist indefinately. Whenever, two phases coexist in equalibrium the chemical potential is

$$\boxed{\mu = 0}. \tag{21}$$

3.2 Part b)

Let's talk about the total energy as an average *i.e.* in terms of the sum all states of the energy in that state times the average occupation number in that state

$$E(T) = \sum_{k,s}\left[\langle n_{k,-}\rangle_{-}\,\epsilon_{+} + \langle n_{k,-}\rangle_{-}\,\epsilon_{-}\right]$$

Since they are fermions only one electron can be in each state and so the average occupation numbers must be simply $\langle n_k\rangle_{-} = 1 - \langle n_k\rangle_{+}$ meaning

$$\begin{aligned}
E(T) &= \sum_{k,s}\left[\langle n_{k,+}\rangle_{-}\,\epsilon_{+} + \left(1 - \langle n_{k,+}\rangle_{-}\right)\epsilon_{-}\right] \\
&= \sum_{k,s}\left[\langle n_{k,+}\rangle_{-}\,\epsilon_{+} - \langle n_{k,+}\rangle_{-}\,\epsilon_{-}\right] + \sum_{k,s}\epsilon_{-}
\end{aligned}$$

The question told us that when the temperature is zero all the negative states are occupied which meanst that the sum of all the negative energy states is the energy at $T = 0$ *i.e.* $\sum_{k,s} \epsilon_- = E(T = 0)$. Plus we know that $\epsilon_- = -\epsilon_+$ and that the degeneracy is two. Using these three pieces of information the energy is

$$\begin{aligned}E(T) &= \sum_{k,s} \left[\langle n_{k,+}\rangle_- \epsilon_+ - \langle n_{k,+}\rangle_- \epsilon_-\right] + \sum_{k,s} \epsilon_- \\ &= 2\sum_{k} \left[\langle n_{k,+}\rangle_- \epsilon_+ + \langle n_{k,+}\rangle_- \epsilon_+\right] + E(0) \\ E(T) - E(0) &= 4\sum_{k} \langle n_{k,+}\rangle_- \epsilon_+\end{aligned}$$

If we take the sum to the continuous limit and substitute in the standard function for $\langle n_{\vec{k}}\rangle_-$ then the energy is

$$\boxed{E(T) - E(0) = 4A\int \frac{d^2\vec{k}}{(2\pi)^2}\frac{\epsilon_+}{e^{\beta\epsilon_+} + 1}} \tag{22}$$

3.3 Part c)

We can determine the value of $E(T) - E(0$ by letting $\epsilon_+ = \hbar v\left|\vec{k}\right| = \hbar v k$ and integrating in polar coordinates.

$$\begin{aligned}E(T) - E(0) &= 4A\int \frac{2\pi k dk}{(2\pi)^2}\frac{\hbar v k}{e^{\beta\hbar v k} + 1} \\ &= \frac{4A}{2\pi}\hbar v\int dk\frac{k^2}{e^{\beta\hbar v k} + 1} \\ &= \frac{4A}{2\pi}\hbar v\int \left(\frac{1}{\beta\hbar v}\right) dx \left(\frac{1}{\beta\hbar v}\right)^2 \frac{x^2}{e^x + 1} \\ &= \frac{2A}{\pi\beta}\left(\frac{1}{\beta\hbar v}\right)^2\int_0^\infty dx\frac{x^2}{e^x + 1}\end{aligned}$$

There's our magical integral function again with $\eta = -1$, $m = 3$ and $z = 1$ meaning that it's another Riemann zeta function.

$$\begin{aligned}E(T) - E(0) &= \frac{2A}{\pi}k_{\mathrm{B}}T\left(\frac{1}{\beta\hbar v}\right)^2 2! f_3^-(1) \\ &= \frac{2A}{\pi}k_{\mathrm{B}}T\left(\frac{k_{\mathrm{B}}T}{\hbar v}\right)^2 2\left(\frac{3}{4}\zeta(3)\right)\end{aligned}$$

$$\boxed{E(T) - E(0) = \frac{3A}{\pi}\zeta(3)\left(\frac{k_{\mathrm{B}}T}{\hbar v}\right)^2 k_{\mathrm{B}}T} \tag{23}$$

3.4 Part d)

Calculate the heat capacity

$$\begin{aligned} C_V &= \left.\frac{\partial E}{\partial T}\right|_V \\ &= \frac{\partial}{\partial T}\left(E(0) + \frac{3A}{\pi}\zeta(3)\left(\frac{k_\mathrm{B}T}{\hbar v}\right)^2 k_\mathrm{B}T\right) \\ &= \frac{3A}{\pi}\zeta(3)\frac{\partial}{\partial T}\left(\frac{k_\mathrm{B}T}{\hbar v}\right)^2 k_\mathrm{B}T \end{aligned}$$

$$\boxed{C_V = \frac{9A}{\pi}k_\mathrm{B}\zeta(3)\left(\frac{k_\mathrm{B}T}{\hbar v}\right)^2} \tag{24}$$

3.5 Part d)

We've been considering electrons with a velocity of $v \approx 10^6 m/s$ but now we would like to know if we need to consider the phonons' contribution to the heat capacity. Now phonons are bosons but they do have the same form of energy

$$\varepsilon = \hbar\nu\,|k|$$

where $\nu \approx 2{\times}10^4 m/s$ is the speed of sound in graphite and also have no chemical potential. The fact that they are bosons means the occupation number changes but if just for a qualitative investigation say it doesn't matter than the treatment of the phonons would be exactly the same and they would have the same form for energy and the same form for heat capacity. The only difference is $v \to \nu$. Since $C_V \propto v^{-2}$ the ratios of their heat capacity would be

$$\begin{aligned} \frac{C_V^{\text{phonon}}}{C_V^{\text{electron}}} &\approx \left(\frac{\nu}{v}\right)^2 \\ &= \left(\frac{2\times 10^4}{10^6}\right)^2 \\ &= 4\times 10^{-4}. \end{aligned}$$

So we expect the electron contribution to be neglible.