6CCP3212 Statistical Mechanics Solutions 2

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1)
(i) Noting that $N = n_\uparrow + n_\downarrow$, we can replace the $n_\downarrow = N - n_\uparrow$, and hence

$$E = n_\uparrow E_\uparrow + n_\downarrow E_\downarrow = \mu H(n_\downarrow - n_\uparrow) = \mu H(N - 2n_\uparrow) \ . \tag{1}$$

Since we have fixed the energy by fixing $n_\uparrow$ and $n_\downarrow$, this is the microcanonical ensemble.
(ii) There are ${}^N C_{n_\uparrow}$ ways of choosing a configuration with $n_\uparrow$ $\uparrow$ dipoles, so

$$\Omega(n_\uparrow) = \frac{N!}{n_\uparrow!(N - n_\uparrow)!} \tag{2}$$

The entropy is $S = k_b \ln \Omega$, which using the Stirling's approximation $\ln p! \approx p \ln p - p$, we get the final answer,

$$S(n_\uparrow) = k_b[N \ln N - n_\uparrow \ln n_\uparrow - (N - n_\uparrow)\ln(N - n_\uparrow)] \ . \tag{3}$$

(iii) They are different because the two entropies are from two different ensembles. The entropy above is derived for fixed E, i.e. it's the entropy for the microcanonical ensemble. The one we derived in class is for fixed T, i.e. for the canonical ensemble.
(iv) The temperature is given by

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial n_\uparrow}{\partial E}\frac{\partial S}{\partial n_\uparrow} = \left(\frac{-k_b}{2\mu H}\right) \ln \frac{N - n_\uparrow}{n_\uparrow} \tag{4}$$

Since $\ln(N - n_\uparrow)/n_\uparrow = \ln(N/n_\uparrow - 1)$, and hence $N/n_\uparrow - 1 > 1$ when $N/n_\uparrow > 2$. The temperature is negative in the limit $n_\uparrow < N/2$. In the case of the canonical ensemble with fixed $T > 0$, we learned from class that under an external H field that is aligned with $\uparrow$, the dipoles are more likely to be in the $\uparrow$ state – this is its *statistical equilibrium* state. However, in the case studied in this problem when $n_\uparrow < N/2$, we have *forced* the lattice of dipoles to mostly in the spin $\downarrow$ state, despite the fact that H is positive. If we now release the system (by removing the forces), and allow it to reach equilibrium with temperature $T > 0$ of the lattice environment, the 2nd law tells that the entropy must increase. From the definition of the temperature $1/T = \frac{\partial S}{\partial E}$, we have

$$dS = \frac{1}{T} dE \ . \tag{5}$$

But going from $n_\uparrow < N/2$ to $n_\uparrow > N/2$ (the equilibrium) means that $dE < 0$ (recall each $\uparrow$ dipole adds negative energy), and $dS > 0$ thus $T < 0$. This phenomenom is called **spin inversion** (or more generally, **population inversion**) – one forces the system far away from its equilibrium state by externally flipping the spins (using a laser for example) opposite to what it would have like to be. Spin inversion requires a lot of energy – we are doing work on the system by flipping each spin – and hence the system becomes *more energetic*. Thus if we stick in a thermometer which measures the "temperature" of the system by its energy, we would find that the thermometer is *very hot*, formally infinitely hot. This is the reason why "negative temperatures" is equivalent to infinite temperature. Spin or population inversions are the fundamental mechanisms by which lasers are constructed.

2)
(i) Since each card is distinct, there are $\Omega = 52!$ ways of arranging 52 distinct cards in a row (i.e. a deck).

(ii) (a) Since the suits are different, there are 26 distinct cards and hence $\Omega = 26!$. (b) Since the suits are identical, there are two identical copies of 13 distinct cards. Thus within the 26! combinations, we need to divide by 2 *per pair* so as not to overcount, and hence $\Omega = 26!/2^{13}$.
(iii) For two identical decks, each card is repeated twice. Thus using the argument in (ii), we have $\Omega = (104!)/2^{52}$.

3)
(i) From

$$\begin{aligned}\langle \Delta E^2 \rangle = \langle (\langle E \rangle - E_r)^2 \rangle &= \langle \langle E \rangle^2 + E_r^2 - 2\langle E \rangle E_r)^2 \rangle \\ &= \langle \langle E \rangle^2 \rangle + \langle E_r^2 \rangle - 2\langle E \rangle \langle E_r \rangle \\ &= \langle E \rangle^2 \rangle + \langle E_r^2 \rangle - 2\langle E \rangle^2 \\ &= \langle E_r^2 \rangle - \langle E \rangle^2 \end{aligned} \tag{6}$$

where we have used the fact that $\langle E \rangle$ is a constant.

But note that

$$\langle E_r^2 \rangle = \frac{1}{Z} \sum_r E_r^2 e^{-\beta E_r} = \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} \left(\sum_r e^{-\beta E_r} \right) = \frac{1}{Z} \left(\frac{\partial^2 Z}{\partial \beta^2} \right) \tag{7}$$

and

$$\langle E \rangle^2 = \left(\frac{\partial \ln Z}{\partial \beta} \right)^2 = \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 \tag{8}$$

so

$$\begin{aligned}\langle E_r^2 \rangle - \langle E \rangle^2 &= \frac{1}{Z} \left(\frac{\partial^2 Z}{\partial \beta^2} \right) - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 \\ &= \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) \\ &= \left(\frac{\partial^2 \ln Z}{\partial \beta^2} \right) . \blacksquare \end{aligned} \tag{9}$$

(ii) From

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \tag{10}$$

since T is intensive, and S is extensive and hence scales as $S \to aS$ under linear rescaling, C_V hence scales as N. $\langle \Delta E^2 \rangle = C_V k_b T^2$ must then scale as N, thus

$$\frac{\langle \sqrt{\Delta E^2} \rangle}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \tag{11}$$

4)
(i)

$$Z = \sum_n e^{-\beta E_n} = \sum_n e^{-\beta(n+1/2)\hbar\omega} = e^{-\beta\hbar\omega/2} \sum_n e^{-n\beta\hbar\omega} \tag{12}$$

(ii) The probability per level n is

$$P_n = \frac{1}{Z} e^{-(n+\frac{1}{2})\hbar\omega/k_b T} . \tag{13}$$

(a) At low temperatures $k_b T \ll \hbar\omega$, so $\hbar\omega/k_b T \gg 1$. The ratio of the probabilities between the n and $n+1$ states is then

$$r = \frac{P_{n+1}}{P_n} = e^{-\hbar\omega/k_b T} \ll 1 \tag{14}$$

thus the higher n states are exponentially suppressed, so only lower n states are occupied.

(b) If only $n = 0$ and $n = 1$ states are occupied, then the partition function is $Z = e^{-\beta E_0} + e^{-\beta E_1}$. The mean energy is then

$$\begin{aligned}\langle E \rangle &= \sum_n P_n E_n \\ &= \frac{1}{Z}\left(\frac{\hbar\omega}{2} e^{-\frac{1}{2}\frac{\hbar\omega}{k_b T}} + \frac{3\hbar\omega}{2} e^{-\frac{3}{2}\frac{\hbar\omega}{k_b T}}\right) \\ &= \frac{1+3r}{2(1+r)}\hbar\omega \ . \end{aligned} \tag{15}$$

(iii) In the general case, using (i), and setting $x = e^{-\beta\hbar\omega}$, we get

$$Z = e^{-\beta\hbar\omega/2} \sum_n x^n = \frac{e^{-\hbar\omega/2k_b T}}{1 - e^{-\hbar\omega/k_b T}} \ , \tag{16}$$

using the geometric series.
The Helmholtz free energy is

$$F = -k_b T \ln Z = \frac{\hbar\omega}{2} + k_b T \ln\left[1 - e^{-\hbar\omega/k_b T}\right] \tag{17}$$

and the entropy

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_V \\ &= -k_b \ln\left[1 - e^{-\hbar\omega/k_b T}\right] + \frac{\hbar\omega}{T}\frac{e^{-\hbar\omega/k_b T}}{1 - e^{-\hbar\omega/k_b T}} \ . \end{aligned} \tag{18}$$

Putting this together, we have $E = F + TS$ from the Helmholtz formula, thus

$$E = \frac{\hbar\omega}{2} + \hbar\omega \frac{e^{-\hbar\omega/k_b T}}{1 - e^{-\hbar\omega/k_b T}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_b T} - 1} \tag{19}$$

(iv) The heat capacity is a straightforward application of the formula.
(v) In the high temperature limit, $k_b T \gg \hbar\omega$, so we can expand

$$e^{\hbar\omega/k_b T} = 1 + \frac{\hbar\omega}{k_b T} + \ldots \tag{20}$$

and plugging this into the result in (iv), we have

$$C_V = k_b \left(\frac{\hbar\omega}{k_b T}\right)^2 \frac{1 + \frac{\hbar\omega}{k_b T}}{(\hbar\omega/k_b T)^2} = k_b\left(1 + \frac{\hbar\omega}{k_b T}\right) \approx k_b \tag{21}$$

since $\hbar\omega/k_b T \ll 1$. For N non-interacting particles in 3D, then this is $C_V = 3Nk_B$.

5)
(i) Each particle is described by 3 quantum numbers. Since there are N non-interacting particles, then each microstate in the ensemble can be described by $3N$ integers.
(ii) Consider a single particle. If we define the "radius"

$$R_0 = \sqrt{p^2 + q^2 + r^2} \tag{22}$$

then all the microstates that are smaller than $E = (\hbar^2\pi^2)/(2ma^2)R_0^2$ is in a 3D sphere with radius R_0. In other words, the energy E defines a radius of this sphere of possible microstates – note that we can use this approximation only in the limit of large E, i.e. the limit where p, q, and r is large. The total number of coordinate points within this sphere is given by the volume

$$V = \frac{4\pi}{3} R_0^3 \propto E^{3/2} \ . \tag{23}$$

Thus, for each particle, the number of microstates with energy less than E must be proportional to V

$$G_1(E) \propto V \propto E^{3/2} \ . \tag{24}$$

For N non-interacting particles, the statistical weight multiply, thus

$$G(E) = \prod_N G_1(E) \propto E^{3N/2} = cE^{3N/2} \ . \blacksquare \tag{25}$$

6)

(i) From

$$\begin{aligned}
S &= k_b \left(\ln Z - \beta \frac{\partial \ln Z}{\partial \beta} \right) \\
&= k_b \left(\ln Z - \frac{1}{k_b T} \frac{\partial T}{\partial \beta} \frac{\partial \ln Z}{\partial T} \right) \\
&= k_b \left(\ln Z + \frac{1}{k_b T} k_b T^2 \frac{\partial \ln Z}{\partial T} \right) \\
&= k_b \frac{\partial}{\partial T} (T \ln Z)
\end{aligned} \tag{26}$$

(ii) This is immediate

$$P = -\left(\frac{\partial F}{\partial V} \right)_T = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \tag{27}$$

(iii) By comparing $đW = -\mu dH \leftrightarrow đW = -PdV$, we can see that by replacing $V \to H$, $P \to \mu$, we get the required result. (μ, H) forms a conjugate pair because the internal energy $dE = TdS - \mu dH$, μ is the intensive variable conjugate to the extensive H.

7)

(i) From

$$\frac{\partial \mathcal{Z}}{\partial \mu} = \sum_r \beta N_r e^{-\beta(E_r - \mu N_r)} \tag{28}$$

so dividing by $\beta \mathcal{Z}$ we get

$$\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = \sum_r N_r \frac{e^{-\beta(E_r - \mu N_r)}}{\mathcal{Z}} = \langle N \rangle \ . \tag{29}$$

The next derivatino follows closely the steps of Q3(i). From $\Delta N = N_r - \langle N \rangle$, we have

$$\langle \Delta N^2 \rangle = \langle N_r^2 \rangle - \langle N \rangle^2 \tag{30}$$

And note that

$$\langle N_r^2 \rangle = \frac{1}{\mathcal{Z}} \sum_r N_r^2 e^{-\beta(E_r - \mu N_r)} = \frac{1}{\mathcal{Z}} \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \left(\sum_r e^{-\beta(E_r - \mu N_r)} \right) = \frac{1}{\mathcal{Z}} \frac{1}{\beta^2} \left(\frac{\partial^2 Z}{\partial \mu^2} \right) \tag{31}$$

and

$$\langle N \rangle^2 = \frac{1}{\beta^2} \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)^2 = \frac{1}{\beta^2} \frac{1}{\mathcal{Z}^2} \left(\frac{\partial Z}{\partial \mu} \right)^2 \tag{32}$$

so

$$\begin{aligned}
\langle N_r^2 \rangle - \langle N \rangle^2 &= \frac{1}{\mathcal{Z}} \frac{1}{\beta^2} \left(\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} \right) - \frac{1}{\beta^2} \frac{1}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)^2 \\
&= \frac{1}{\beta^2} \frac{\partial}{\partial \mu} \left(\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} \right) \\
&= \frac{1}{\beta^2} \left(\frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2} \right) . \blacksquare
\end{aligned} \tag{33}$$

(ii) In the case of fixed V and S, then $dS = 0$ and $đW = -PdV = 0$, we get

$$dE = \mu dN \tag{34}$$

and hence $\left(\frac{\partial E}{\partial N}\right)_{V,S} = \mu$.

(iii) We follow the derivation in the class (see lecture notes section 2.4), but with additional pairs of conjugate variables $(\mu^{(i)}, N^{(i)})$. The probability of finding of a microstate r is

$$P_r = \text{const} \times \Omega_B(E_0 - E_r, \{N_0^{(i)} - N_r^{(i)}\}) \tag{35}$$

where $\{N_0^{(i)} - N_r^{(i)}\}$ is the set of all possible $N_0^{(1)} - N_r^{(1)}$,$N_0^{(2)} - N_r^{(2)}$, etc. Using the formula for the entropy for the microcanonical ensemble $S_B = k_b \ln \Omega_B$, we then have

$$S_B(E_0 - E_r, \{N_0^{(i)} - N_r^{(i)}\}) = S_B(E_0, \{N_0^{(i)}\}) - \left(\frac{\partial S_B}{\partial E_0}\right)_{E_0,\{N_0^{(i)}\}} dE_r - \sum_{n=1}^{n=i} \left(\frac{\partial S_B}{\partial N_0^{(n)}}\right)_{E_0,\{N_0^{(i)}\}} dN_r^{(n)} + \ldots \tag{36}$$

and hence following section 2.4, we can define the

$$\mu_i = -T\left(\frac{\partial S_B}{\partial N_0^{(i)}}\right)_{E_0,\{N_0^{(i)}\}} . \tag{37}$$

8)

(i) The partition function is

$$Z = \sum_r e^{-\beta E_r} = 1 + e^{-\beta E_-} + e^{-\beta E_+} = 1 + 2e^{-\beta\epsilon} \tag{38}$$

The probabilities are then

$$P_0 = \frac{1}{Z} \ , \ P_\pm = \frac{1}{Z}e^{-\beta E_\pm} = \frac{1}{Z}e^{-\beta\epsilon} \tag{39}$$

In the high temperature limit $k_bT \gg \epsilon$, or $\beta\epsilon \ll 1$, $e^{-\beta\epsilon} \to 1$, so $Z \to 3$ and thus $P_\pm = P_0 =\to (1/3)$ – they are all equally likely. This makes sense since at high temperatures, the energy fluctuations is too strong for the interactions of the nucleus with the electric charge distribution to hold the spin. In the low temperature limit, $\beta\epsilon \gg 1$, $e^{-\beta\epsilon} \to 0$, so $Z \to 1$, and $P_0 \to 1$, $P_\pm \to 0$. So the nuclei wants to be in the 0 spin state.

(ii) The mean energy is given by

$$\begin{aligned} E_1 &= \sum_r P_r E_r \\ &= \frac{1}{Z}(E_+ e^{-\beta E_+} + E_- e^{-\beta E_-}) \\ &= \frac{2\epsilon e^{-\beta\epsilon}}{1 + 2e^{-\beta\epsilon}} \\ &= \frac{2\epsilon}{e^{\beta\epsilon} + 2} . \end{aligned} \tag{40}$$

(iii) For N non-interacting nuclei, the partition function multiply so

$$Z_N = \prod_N Z = \left(1 + 2e^{-\beta\epsilon}\right)^N \tag{41}$$

The mean energy is

$$E_N = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{2N\epsilon}{e^{\beta\epsilon} + 2} \tag{42}$$

and the entropy is

$$S = k_b(\ln Z_N + \beta E_N) = k_b N \left(\ln(1 + 2e^{-\beta\epsilon}) + \frac{2\beta\epsilon}{e^{\beta\epsilon} + 2} \right) . \tag{43}$$

In the high temperature limit where $k_b T \gg \epsilon$, $S = k_b N(\ln(1+2)) = k_b \ln 3^N$ – the nuclei spins are random so there are 3^N microstates. This is a microcanonical ensemble with a fixed energy $E = 2N\epsilon/(e^{\beta\epsilon} + 2) \to (2/3)N\epsilon$. In the low temperature limit where $k_b T \ll \epsilon$, $S = k_b(\ln 1) = 0$ – there is only one configuration where all the spins are at the 0 state. This is a microcanonical ensemble with fixed energy $E = 2N\epsilon/(e^{\beta\epsilon} + 2) \to 0$.