6CCP3212 Statistical Mechanics Homework 2

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1) (**Paramagnet and negative temperature**.) Consider a lattice of N non-interacting magnetic spin-1/2 dipoles with spins $\uparrow$ and $\downarrow$. Under an external magnetic field $H > 0$ that is parallel with the spin $\uparrow$ direction, some of the dipoles will be parallel $\uparrow$ or anti-parallel $\downarrow$ with the magnetic field, with the energy

$$E_\uparrow = -\mu H \ , E_\downarrow = \mu H \ , \tag{1}$$

where μ is the magnetic moment per dipole.
(i) Consider the ensemble of microstates such that there are fixed $n_\uparrow$ and $n_\downarrow$ dipoles. Show that the energy of the system as a function of $n_\uparrow$ is

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

What ensemble does this define?
(ii) Express the statistical weight of the system as a function of $n_\uparrow$ and hence show that the entropy of the system is given by

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

(iii) Compare this result to the one we obtained in class by considering the partition function

$$S = k_b N[\ln 2 + \ln\cosh(\beta\mu H) - \beta\mu H \tanh(\beta\mu H)] \ , \tag{4}$$

which we obtained by calculating the partition function and using $S = k_b(\ln Z + \beta\bar{E})$. Why is it different from our result above?
(iv) Calculate the temperature of the system

$$\frac{1}{T} = -\frac{k_b}{2\mu H}\ln\frac{N - n_\uparrow}{n_\uparrow} \ . \tag{5}$$

and hence show that the temperature is negative when $n_\uparrow < N/2$. Explain why this is so, by comparing this result to the case of the canonical ensemble with some fixed, positive T we studied in class (this is hard, but give it a shot before looking at the solutions!)

2) A deck of cards have 4 suits ($\heartsuit$, $\spadesuit$, $\diamondsuit$, $\clubsuit$) of 13 cards each (from A, 2, 3, ..., 10, J, Q, K) for a total of 52 cards.
(i) Let Ω be the total number of possible unique ways a deck of cards be shuffled. By considering each unique shuffled deck as a microstate, Ω is then the statistical weight of the system. Calculate Ω for a deck of cards.
(ii) Consider two suits of 13 cards each, which are then shuffled together. What is the statistical weight of the shuffled decks if (a) the suits are different (say $\diamondsuit$ and $\clubsuit$) and (b) the suits are identical (say $\diamondsuit$ and $\diamondsuit$)?
(iii) Finally if we combine two identical decks of cards of 4 suits each, argue that the statistical weight of the combined deck is given by

$$\Omega_T = \frac{1}{2^{52}}(104!) \ . \tag{6}$$

3) For a canonical ensemble, the partition function is given by

$$Z = \sum_r e^{-\beta E_r} \tag{7}$$

where r labels the microstates, and E_r is the energy of microstate r.
(i) The mean energy is the ensemble average

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} \ . \tag{8}$$

The energy deviation from mean for each microstate is defined as $\Delta E_r \equiv \langle E\rangle - E_r$. Show that the ensemble average of the square deviation is

$$\langle \Delta E^2\rangle = \left(\frac{\partial^2 \ln Z}{\partial \beta^2}\right) \ . \tag{9}$$

(*Hint*: Use the fact that the ensemble average of linear terms is also linear, i.e. $\langle X+Y\rangle = \langle X\rangle + \langle Y\rangle$.)
(ii) In class, we show that the fluctuation $\langle \Delta E^2\rangle = C_V k_b T^2$. Argue that

$$\frac{\langle\sqrt{\Delta E^2}\rangle}{\langle E\rangle} \sim \frac{1}{\sqrt{N}} \ . \tag{10}$$

($Hint$: Show that C_V is an extensive quantity.)

4) Consider a 1-dimensional quantum simple harmonic oscillator. From your quantum mechanics course, you learned that the energy spectrum is given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \ , \tag{11}$$

where $\omega > 0$ is the characteristic frequency of the oscillator, and $n = 0, 1, 2, \ldots$ is the principal quantum number. The oscillator is in thermal contact with a heat bath of temperature T.
(i) Write down the partition function of this ensemble.
(ii) Consider the *low* temperature case, $k_b T \ll \hbar\omega$. Argue that only the states with small n are expected to be occupied. If we assume that only the $n = 0$ and $n = 1$ states are occupied, calculate (a) the ratio of $r \equiv P_1/P_0$ (i.e. the ratios of the probabilities) and (b) the mean energy $\langle E\rangle$ of the oscillator as a function of temperature and r.
(iii) Consider now the general case where the temperatures can be of any amplitude. Show that the partition function in this case can be written as

$$Z = \frac{e^{-\hbar\omega/2k_bT}}{1 - e^{-\hbar\omega/k_bT}} \ . \tag{12}$$

($Hint$: The geometric series $\sum_0^\infty x^n = 1/(1-x)$ may be useful.)
Using this result, calculate the Helmholtz free energy F and the entropy S, and hence show that the ensemble average of the energy is

$$E = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_bT} - 1} \ . \tag{13}$$

(iv) Again considering the general case, use the results of (iii) to show that the heat capacity is

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = k_b\left(\frac{\hbar\omega}{k_bT}\right)^2 \frac{e^{\hbar\omega/k_bT}}{(e^{\hbar\omega/k_bT} - 1)^2} \ . \tag{14}$$

(v) Now consider the *high* temperature limit $k_bT \gg \hbar\omega$. Use the result in (iv) to show that the heat capacity in this limit is

$$C_V = k_b \ . \tag{15}$$

($Hint$: You might want to expand e^x for $x \ll 1$.)
If we consider a solid with N particles which can vibrate in 3 dimensions, this results in the heat capacity of $C_V = 3Nk_b$, which is known as the **Dulong-Petit law** – a result which was first observed experimentally. The derivation that you have just done is proposed by Einstein.

5) A quantum mechanical particle in a 3-D infinite square well with $0 \leq x, y, z \leq a$ has eigenstates with energy

$$E = \frac{\hbar^2 \pi^2}{2ma^2}(p^2 + q^2 + r^2) \ , \tag{16}$$

where $p, q, r \in \mathbb{Z}$ (i.e. positive integers).

(i) Suppose we put in N such *non-interacting* particles in the same box which are indistinguishable. Argue that each microstate of this system is parameterized by $3N$ integers.

(ii) Let $G(E)$ be the number of microstates with energy less than E. Show that, for $E \gg \hbar^2\pi^2/(2ma^2)$,

$$G(E) = cE^{(3N/2)} \tag{17}$$

for some positive constant c.

(Hint: In the limit $E \gg \hbar^2\pi^2/(2ma^2)$, one can consider the quantum numbers (p, q, r) as coordinates, with each grid point in this coordinate a possible microstate. So one can define $R_0^2 = p^2 + q^2 + r^2$, and compute the total number of coordinates as a 3D sphere via a volume integral.)

6) In class, we showed that the entropy of a canonical ensemble is given by

$$S = k_b \left(\ln Z - \beta \frac{\partial \ln Z}{\partial \beta} \right) \ , \tag{18}$$

where the partition function is

$$Z = \sum_r e^{-\beta E_r} \ . \tag{19}$$

(i) Show that the entropy can be expressed as

$$S = k_b \frac{\partial}{\partial T}(T \ln Z) \ . \tag{20}$$

(ii) If we allow the volume of the canonical ensemble to change, the partition function Z is then a function of both β and V, i.e. $Z(\beta, V)$. We have shown in class that Helmholtz free energy is given by

$$F = -k_b T \ln Z \ . \tag{21}$$

Using this and the identity we derived in Chapter 1

$$P = -\left(\frac{\partial F}{\partial V} \right)_T \ , \tag{22}$$

show that this leads to the relation

$$P = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \ . \tag{23}$$

(iii) The partition function Z for a system of magnetic dipoles is a function of β and its magnetic field H. We can define the work done on the system to be

$$đW = -\mu dH \tag{24}$$

where μ is the mean magnetic moment. Using the results in (ii), show that

$$\mu = \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} \ . \tag{25}$$

Argue that (μ, H) forms a conjugate pair of state variables.

7) (**The grand canonical ensemble**.) The grand canonical ensemble is the set of microstates at constant V, T and μ, with the partition function

$$\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)} \tag{26}$$

and probability per microstate r

$$P_r \equiv \frac{e^{-\beta(E_r-\mu N_r)}}{\mathcal{Z}} \ . \tag{27}$$

(i) Show that the mean particle number and its dispersion with $\Delta N \equiv \langle N\rangle - N_r$ are given by

$$\langle N\rangle \equiv \sum_r P_r N_r = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mu} \ , \tag{28}$$

and

$$\langle \Delta N^2\rangle = \frac{1}{\beta^2}\frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2} = \frac{1}{\beta}\frac{\partial \langle N\rangle}{\partial \mu} \ . \tag{29}$$

(ii) In class, we showed that

$$dS = \beta(-đW + dE - \mu dN) \ . \tag{30}$$

Show that this implies the thermodynamical definition of the chemical potential

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{V,S} \ . \tag{31}$$

(iii) Suppose a system consists of i non-interacting species, with $N^{(i)}$ particles per species and corresponding chemical potential μ_i. This system is immersed into an environment B with temperature T and particles $N_B^{(i)}$ such that the total $N_0^{(i)} = N_B^{(i)} + N_r^{(i)}$ is conserved. The partition function of this system is given by

$$\mathcal{Z} = \sum_r e^{-\beta(E_r - \sum_i \mu_i N_r^{(i)})} \ . \tag{32}$$

Show that the chemical potential is given by

$$\mu_i = -T\left(\frac{\partial S_B}{\partial N_0^{(i)}}\right)_{E_0,\{N_0^{(i)}\}} \tag{33}$$

where $\{N_0^{(i)}\} = \{N_0^{(1)}, N_0^{(2)}, N_0^{(3)}, \dots\}$ is the set of all particle species and $S_B = k_b \ln \Omega_B(E_0 - E_r, N_0^{(1)} - N_r^{(1)}, N_0^{(2)} - N_r^{(2)}, \dots, N_0^{(i)} - N_r^{(i)})$.

8) The nuclei of atoms of a crystalline solid have spin 1 that are non-interacting. The spin-statistics theorem then tells us that each nuclei can take 3 possible spin states, $+, 0, -$. In the presence of an ellipsoidal electric charge distribution, each nuclei obtain the following energies

$$E_- = E_+ = \epsilon \ , E_0 = 0 \ . \tag{34}$$

(i) Consider a single nucleus in a "bath" of nuclei with fixed temperature T. Calculate the probabilities P_0, $P_\pm$ of the three spin states. What are the most likely states when $k_bT \gg \epsilon$ and when $k_bT \ll \epsilon$?
(ii) Calculate the mean energy of a single nucleus and show that it is

$$E_1 = \frac{2\epsilon}{e^{\beta\epsilon}+2} \ . \tag{35}$$

(iii) Consider a lattice of N such nuclei. Write down the partition function of the system and hence calculate the mean energy E_N, and entropy S of the system.
(iv) Using your results in (iii), show that the entropy of a lattice of N nuclei in the high temperature limit $k_bT \gg \epsilon$ is $S = k_b \ln 3^N$. What is the entropy of the low temperature limit $k_BT \ll \epsilon$? Explain this result in terms of the microcanonical ensemble.