Physics 210- Fall 2018

Classical and Statistical mechancis

Solution: Home Work # 4
Posted on 11 December, 2018

1. In the canonical ensemble we saw that

$$F = -kT \log Z, \quad Z = \sum_n e^{-\beta \varepsilon_n},$$

where ε_n are the eigenvalues of the N particle system. Similarly for the Grand Canonical Ensemble, we saw

$$\Omega = -kT \log Z, \quad Z = \sum_{n, N_n} e^{-\beta(\varepsilon_n - \mu N_n)},$$

a) Show that

$$\bar{N^2} - \bar{N}^2 = \alpha \, \frac{d\bar{N}}{d\mu},$$

with a suitable α. From this show that the mean value $\bar{N}$ is very close to being sharp. (We discussed this in class, I would like you to fill in the details). ...[15]

Let us note that for any value of r the average is defined as:

$$\bar{N^r} = \frac{\sum_{n,N_n} N_n^r e^{-\beta(\varepsilon_n - \mu N_n)}}{\sum_{n,N_n} e^{-\beta(\varepsilon_n - \mu N_n)}} = \frac{\partial^r_{\beta\mu} Z}{Z}.$$

From this it follows that

$$\bar{N} = \partial_{\beta\mu} \log Z$$

and

$$\partial_{\beta\mu} \bar{N} = \bar{N^2} - \bar{N}^2.$$

We can rewrite the left hand side as $k_B T \partial_\mu \bar{N}$.

What this means is that in the grand canonical ensemble we will find $\bar{N^2}$ to be $\bar{N}^2$, a large term of $O(N^2)$ plus a correction $\partial_{\beta\mu}\bar{N}$, which is only of the $O(N)$. Hence the number of particles is sharp as $N \to \infty$.

b) Show that as $T \to 0$ the variable

$$F - E$$

vanishes, from the property of $E = \bar{\varepsilon}_n$ and the definition of F. ...[10]

We recall that $F = -k_B T \log Z$ and from the definition of the partition function, $\bar{E} = -\partial_\beta \log Z$. We may therefore write

$$\bar{E} = \partial_\beta \beta F = F - T\partial_T F,$$

where we used $\beta\partial_\beta = -T\partial_T$. Hence

$$\bar{E} - \partial_\beta \beta F = -T\partial_T F.$$

The right hand side vanishes as $T \to 0$ provided $-\partial_T F$ is non-singular. In fact $-\partial_T F$ is the entropy S and vanishes at $T = 0$ by the third law. Hence the required result.

2. a) Using the N spin half problem

$$H = -B\sum_j \sigma_j,$$

with $\sigma_j = \pm 1$, calculate the partition function $Z = \sum_{\sigma_j} e^{-\beta H}$, and the free energy F. ...[5]

We calculate as follows

$$Z = \sum_{\cdots\sigma_j\cdots} e^{\beta B \sum_i \sigma_i} = (2\cosh(\beta B))^N, \quad F = -Nk_B T \log(2\cosh(\beta B)).$$

b) Calculate the magnetization $M = -dF/dB$ and susceptibility $\chi = dM/dB/_{B\to 0}$. ...[10]

By straightforward differentiation at finite B we get

$$M = N \tanh \beta B,$$
$$\chi = dM/dB\big|_{B\to 0} = N\beta \cosh^{-2}(\beta B)\big|_{B\to 0} = N\beta.$$

c) Calculate the specific heat C as a function of T. ...[5]

We use $C = d\bar{E}/dT$ and

$$\bar{E} = \partial_\beta \beta F = -NB \tanh \beta B,$$

and hence

$$C = Nk_B \frac{B^2}{(k_B T)^2} \frac{1}{\cosh^2 \beta B}.$$

d) Discuss briefly the $T = 0$ limit of C and χ. ...[5]

We see that χ diverges as $T \to 0$ when we set $B = 0$, whereas it is finite if we leave B non-zero. The heat capacity C vanishes as $B \to 0$ and also as $B \to \infty$ at any non-zero T. As $T \to 0$ we see that $C \to 0$.

3. Consider the ideal gas of non-interacting particles in the grand canonical ensemble. We can write

$$\Omega(T, \mu, V) = -k_B T \log\{\sum_{N=0}^{\infty} e^{\beta \mu N} Z_N(T, V)\}$$

where Z_N is the canonical partition function

$$Z_N = \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3 q_i d^3 p_i}{h^3} \, e^{-\beta \sum_i \frac{p_i^2}{2m}}.$$

a) Show that

$$Z_N = \frac{1}{N!} \left(\frac{V}{\lambda_{th}^3} \right)^N$$

where $\lambda_{th} = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength. ...[10]

We note that in Z_N the integration over the different particles decouple so we can write

$$Z_N = \frac{1}{N!} \Phi^N,$$

where

$$\Phi = \int \frac{d^3 q d^3 p}{h^3} e^{-\beta \vec{p}.\vec{p}/(2m)}.$$

We can further decouple the three components of $\vec{p}$ and write this as

$$\Phi = \frac{V}{h^3} \phi^3; \; \phi = \int dp e^{-\beta p^2/(2m)} = \sqrt{2\pi m k_B T},$$

so

$$\Phi = \frac{V}{\lambda_T^3}.$$

and hence

$$Z_N = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N$$

b) Carry out the sum over N exactly and show that the grand potential

$$\Omega = -k_B T e^{\beta\mu}\frac{V}{\lambda_{th}^3}.$$

...[5]

$$Z_{GC} = \sum_N Z_N e^{\beta\mu N} = \sum_N \frac{1}{N!}\left(e^{\beta\mu}\frac{V}{\lambda_T^3}\right)^N = e^{\left\{e^{\beta\mu}\frac{V}{\lambda_T^3}\right\}}.$$

Using $\Omega = -k_B T \log Z_{GC}$ the required result follows.

c) From Ω calculate expressions for $\bar{N}, P$ in terms of μ, T and V. ...[5]

From thermodynamics

$$d\Omega = -S\,dT - p\,dV - N\,d\mu$$

and hence

$$p = -\partial_V\Omega = k_B T\frac{e^{\beta\mu}}{\lambda_T^3},$$

$$\bar{N} = -\partial_\mu\Omega = V\frac{e^{\beta\mu}}{\lambda_T^3},$$

d) By inversion find μ as a function of density and T. ...[5]

This is obvious from the above result for $\bar{N}$. Dividing and taking logs we get:

$$\mu = k_B T \log n\lambda_T^3.$$

4. Consider a set of N quantum harmonic oscillators

$$H = \sum_{i=1}^{N}\hbar\omega(n_i + \frac{1}{2})$$

a) Calculate the partition function Z by summing $e^{-\beta H}$ over all n_i. ...[15]

$$Z = \sum_{\cdots n_i \cdots} e^{-\beta\hbar\omega(n_i+\frac{1}{2})} = \prod_i \left(\sum_{n_i=0,1,2,..} e^{-\beta\hbar\omega(n_i+\frac{1}{2})} \right) = \frac{1}{(2\sinh\frac{\beta\hbar\omega}{2})^N}$$

where we used the geometric sum formula.

b) From this calculate the average energy E, and specific heat C as functions of T,N. ...[5]

Let us use

$$E = \partial_\beta \beta F = N\frac{\beta\hbar\omega}{2}\coth\frac{\beta\hbar\omega}{2}.$$

We may calculate the heat capacity from this using

$$C = \partial_T E = \frac{N}{k_B T^2}(\frac{\beta\hbar\omega}{2})^2 / \sinh^2\frac{\beta\hbar\omega}{2}$$

c) Find the probability $p(n)$ that a particular oscillator is in its nth quantum level. ...[5]

For a particular oscillator i_0 say, we can define the probability of an excited state n_i by summing over all other variables. Using the factorization (i.e. independence) of all sites we thus obtain

$$p(n_i) = \frac{\exp -\beta\hbar\omega(n_i+\frac{1}{2})}{\sum_{n_i=0,1,...}\exp -\beta\hbar\omega(n_i+\frac{1}{2})} = e^{-\beta\hbar\omega n_i}\left(1 - e^{-\beta\hbar\omega}\right).$$

5. *This is optional. This is a type of problem that you might encounter in actual experimental physics, and for that reason also in the quals*

An experiment on the heat capacity was performed on a unknown amount of La_2CuO_4, and the resulting data for a large range of T was fit very well to

$$C = \frac{k_B^2 T}{\Delta}\text{sech}^2\frac{k_B T}{\Delta} \times c_0,$$

where the dimensionless constant $c_0 = 1.025 \times 10^{24}$, and the constant $\Delta = 10$K. Assume that the heat capacity is purely from non-interacting Copper spins (each atom has a spin half), and neglecting phonons, compute the entropy at $T \gg \Delta/k_B$, and from this find the mass of the system.

{Required Data: Atomic weight of Oxygen=16, Cu=63.5,La=139. You will need to argue that each mole containing the Avogadro number of formula units has a known number of copper spin half particles. You will also need to make an educated guess about the entropy of these spins. }