Some Questions On Statistical Physics[‡]

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Contents

Section-A

Question-A1: At constant volume and particle number, what does the derivative of the entropy S with respect to the energy E equal?

Solution:

Since the deviation of the system energy (denoted as U) can be written as:

$$dU = TdS - PdV \tag{1}$$

when the volume of the system is kept as constant, then we will definitely have:

$$dU = TdS \tag{2}$$

Then it is straightforward that:

$$\frac{dS}{dE} = \frac{1}{T} \tag{3}$$

Q.E.D.

Question-A2: In the canonical ensemble, a computation of the N-particle partition function in a particular example reveals that $Z_N = aV^N T^{3N}$, where a is a constant independent of the volume V and temperature T. what is C_V, the specific heat at constant volume, for this system?

Solution:

The N-particle canonical partition function has been given as $Z_N = aV^N T^{3N}$, then the average energy of the system can be calculated:

$$\langle E \rangle = -\frac{1}{Z_N}(\frac{\partial Z_N}{\partial \beta})_{N,V} \tag{4}$$

$$\text{where } \beta \equiv \frac{1}{k_B T}(k_B \rightarrow Boltzmann\ Constant)$$

$$\Longrightarrow$$

$$\begin{aligned}\langle E \rangle &= -\frac{1}{aV^N T^{3N}}\Big[\frac{\partial(aV^N T^{3N})}{\partial(\frac{1}{k_B T})}\Big]_{V,N} \\ &= -\frac{aV^N}{aV^N T^{3N}}\Big[\frac{\partial(T^{3N})}{-\frac{1}{k_B T^2}\partial T}\Big]_{V,N} \\ &= \frac{k_B T^2}{T^{3N}} \cdot \frac{\partial(T^{3N})}{\partial T} = 3Nk_B T \end{aligned} \tag{5}$$

Therefore the specific heat C_V can be derived:

$$\begin{aligned} C_V &= \Big(\frac{\partial \langle E \rangle}{\partial T}\Big)_{V,N} \\ &= \Big[\frac{\partial(3Nk_B T)}{\partial T}\Big]_{V,N} \\ &= 3Nk_B \end{aligned} \tag{6}$$

Q.E.D.

Question-A3: A system in the microcanonical ensemble has 137 microstates consistent with a particular energy E_0. According to the fundamental assumption of statistical mechanics, if we measure the energy of the system to be E_0, what is the probability that the system is in any particular one of these microstates?

Solution:

For the microcanonical ensemble, there is no energy and particle transfer between each component of the ensemble. If there are M microstates consistent with a particular energy, which means the degeneracy of corresponding energy is M, then all the microstates are distributed with the same probability — 1/M. Thus the answer to this question is 1/137.

Q.E.D.

Question-A4: Consider a particle which can have energies $E_n = n\epsilon$ for any $n = 0, 1, 2, 3, \cdots$. In the canonical ensemble, what is the partition function Z_1 of this one-particle system?

Solution:

The 1-particle canonical partition is given as:

$$\begin{aligned} Z_1 &= \sum_s e^{-\beta E_s} \\ &= \sum_{n=0}^{\infty} e^{-n\beta\epsilon} \end{aligned} \tag{7}$$

where $\beta = 1/k_B T$ and k_B is Boltzmann constant. To calculate (7), we need the formula to calculate the sum of Geometric progression. For example, if we are given the following sum to calculate:

$$S = a_1 + a_1 q + a_1 q^2 + \cdots + a_1 q^n = \sum_{i=0}^{n} a_1 q^i \tag{8}$$

The corresponding formular is:

$$S = \frac{a_1(1 - q^n)}{1 - q} \tag{9}$$

Here in this specific question, we have $a_1 = 1$ and $q = e^{-\beta\epsilon}$, thus the 1-particle canonical partition function is:

$$\begin{aligned} Z_1 &= \sum_{n=0}^{\infty} e^{-n\beta\epsilon} \\ &= \lim_{n\to\infty} \frac{1 - e^{-n\beta\epsilon}}{1 - e^{-\beta\epsilon}} && (10) \\ &= \frac{1}{1 - e^{-\beta\epsilon}} && (11) \end{aligned}$$

Here it should be pointed out that $n \to$ indicates all the possible states are included. And since both β and ϵ are with finite value, thus when $n \to \infty$ the term $e^{-n\beta\epsilon}$ in the numerator of (10) becomes 0.

Q.E.D.

Question-A5: Consider a system of N independent magnetic dipoles with magnetic moments $\vec{\mu}$ in an external magnetic field $\vec{H}$. What is the average magnetization $\langle M \rangle$ of this system at $T = 0$ and $T = \infty$?

Solution:

First of all, the expression for the average magnetization $\vec{M}$ of the system is given by:

$$\vec{M} = \sum \vec{\mu} \tag{12}$$

which is the vector summation of the magnetic moments of all the magnetic dipoles. When all the magnetic dipoles are put in an external magentic field $\vec{H}$, the orientation of the magnetic moment of each magnetic dipole should be definitely influenced by $\vec{H}$. Basically, each magnetic dipole tends to point to the direction of the external magnetic field due to the magnetic force. However, there also exists the influence of the thermal vibration which tends to violate the normal orientation (along the external magnetic field) of the magnetic dipoles. More importantly, this kind of violation due to thermal effect increases with the increasing of temperature. When $T = 0$, there is no thermal violation at all, thus all the magnetic dipoles are aligned up along the external magnetic field and the average magnetization can be calculated:

$$\langle M \rangle = \sum_N \vec{\mu} = N\vec{\mu}\Big|_{T=0} \tag{13}$$

When $T \to \infty$, the thermal vibration dominates the system and totally cover the effect of the external magnetic field, which means all the magnetic dipoles are then randomly oriented. Therefore, if taking an overall look at the whole system, for each magnetic dipole, there will always exist another magnetic dipole with the opposite orientation, which will then cancel out the total magnetization. Thus overall speaking, the average magnetization is 0, i. e.:

$$\langle M \rangle = 0\Big|_{T\to\infty} \tag{14}$$

Q.E.D.

Question-A6: Given the Maxwell celocity distribution

$$F(v)dv = 4\pi(\frac{m}{2\pi k_B T})^{3/2} v^2 e^{-mv^2/2k_B T} dv \tag{15}$$

find the *most probable* speed of a particle.

Solution:

Given the Maxwell velocity distribution (15), then finding the *most probable* speed of a particle is equivalent to find at what speed v_m will function $F(v)$ be maximized. Thus we should have;

$$\frac{dF(v)}{dv}\Big|_{v_p} = 0 \tag{16}$$

The differentiation of $F(v)$ is given by:

$$\begin{aligned}
\frac{dF(v)}{dv} &= \frac{d}{dv}\Big[4\pi(\frac{m}{2\pi k_B T})^{3/2} v^2 e^{-mv^2/2k_B T}\Big] \\
&= 4\pi(\frac{m}{2\pi k_B T})^{3/2} \frac{d}{dv}\Big(v^2 e^{-mv^2/2k_B T}\Big) \\
&= 4\pi(\frac{m}{2\pi k_B T})^{3/2} \big[2ve^{-mv^2/2k_B T} + v^2(\frac{-m}{2k_B T} e^{-mv^2/2k_B T})2v\big] \\
&= 4\pi(\frac{m}{2\pi k_B T})^{3/2} e^{-mv^2/2k_B T}(2v - 2v^3 \frac{m}{2k_B T})
\end{aligned} \tag{17}$$

Combining (16) and (17) will give us:

$$\frac{dF(v)}{dv}\Big|_{v_p} = 4\pi(\frac{m}{2\pi k_B T})^{3/2} e^{-mv_p^2/2k_B T}(2v_p - 2v_p^3 \frac{m}{2k_B T}) = 0$$

$$\Longrightarrow$$

$$2v_p - 2v_p^3 \frac{m}{2k_B T} = 0 \tag{18}$$

Therefore finally we have the expression for *most probable* speed v_p of a particle (following Maxwell distribution):

$$v_p = \sqrt{\frac{2k_B T}{m}} \tag{19}$$

Q.E.D.

Question-A7: What is the relationship between the density $n \equiv N/V$ and the thermal wavelength λ that determines the regime in which it is necessary to take into account the quantum effects?

Solution:

The thermal wavelength of the system is given by λ, and when the inter-particle distance is comparable to (or smaller than) λ, it is necessary to take into account of the quantum effects. Since the density is given by $n = N/V$, the space taken up by each particle is then $1/n = V/N$. Thus the average inter-particle distance is $(V/N)^{1/3}$, if imagining the space taken up by each particle as a cubic. Thus we should have the condition to take into account of the quantum effects:

$$(1/n)^{1/3} \leq \lambda \tag{20}$$

Q.E.D.

Question-A8: For a system in which the mean occupation number $\langle n_E \rangle$ is given by $\langle n_E \rangle = (e^{(E-/mu)/k_B T} + a)^{-1}$, whch different values of a describe Bose-Einstein, Fermi-Dirac and Maxwell-Boltamann statistics?

Solution:

First of all, the formula of the three different kinds of distribution are given. For a collection of distinguishable particles follow the Maxwell-Boltzmann distribution, and the mean occupation number is given as:

$$\langle n_E \rangle = \frac{N}{Z} e^{-\frac{E}{k_B T}} \tag{21}$$

For a collection of indistinguishable fermions, the Fermi-Dirac distribution is given by:

$$\langle n_E \rangle = \frac{g_E}{e^{\frac{E-\mu}{k_B T}} + 1} \tag{22}$$

where g_E is the degeneracy of state corresponding to energy E, and μ is the chemical potential.
Finally for a collection of indistinguishable bosons, the Bose-Einstein distribution is given as:

$$\langle n_E \rangle = \frac{g_E}{Be^{\frac{E}{k_B T}} - 1} \tag{23}$$

Therefore the answer to the question is straightforward:

$$a = 0 \rightarrow \text{Maxwell-Boltzmann statistics}$$
$$a = 1 \rightarrow \text{Fermi-Dirac statistics}$$
$$a = -1 \rightarrow \text{Bose-Einstein statistics}$$

Q.E.D.

Question-A9: In a typical blackbody (aka "photon gas"), the energy scales with which power of the temperature?

Solution:

According to Stefan-Boltamann law, the answer to the question is: the energy of a typical blackbody scales with the 4th power of temperature, i.e. $E \propto T^4$.

Q.E.D.

Question-A10: In a system of N spin-3/2 particles at zero temperature, what is the maximum number of particles that can occupy the zero-energy state of the system?

Solution:

The system in the question is a typical collection of indistinguishable Fermions (with half-integer spin). Thus first of all, each single state can only hold one particle. Then for any given energy state, all particles at that energy state should be with different spin from each other (no more particles are allowed). - Pauli expulsion principle.
When $T = 0$, the system is at its ground state, so all the particles are just placed at different energy state (from low to high) continously, meanwhile at each energy state (e.g. the zero-energy state), all particles should be with different spin. Thus the maximum number of particles that can occupy the zero-energy state of the system is 4.
The reason is, for spin-3/2 particle, the 'spin value' (exactyl speaking, should be the projection of spin on z-axis) can be $\pm 1/2$ and $\pm 3/2$, and the total number of possible 'spin value' is $N_s = 2s + 1 = 4$.

Q.E.D.

Section-B

Question-B1

a) Consider a system of N distinguishable one-dimensional oscillators, each of which has energy

$$E(p.q) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2, \tag{24}$$

where p is the momentum, q is the displacement, and m and ω are the characteristic mass and frequency, Calculate Z_1, the classical one-particle (canonical) partition function of this system.

Solution:

The one-particle canonical partition function is given by:

$$Z_1 = \sum_s e^{-\epsilon_s \beta}, \text{ where } \beta = 1/k_B T \tag{25}$$

The state energy is given by (24), thus we have the one-particle canonical partition function as:

$$\begin{aligned}
Z_1 &= \int_{-\infty}^{\infty} e^{-E/k_BT} dqdp \\
&= \int_{-\infty}^{\infty} exp\Big(-\frac{\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2}{k_BT}\Big) dqdp \\
&= \int_{-\infty}^{\infty} exp(-\frac{1}{2mk_BT}p^2)dp \int_{-\infty}^{\infty} exp(-\frac{m\omega^2}{2k_BT}q^2)dq \\
&= \sqrt{2mk_BT\pi} \cdot \sqrt{\frac{2k_BT}{m\omega^2}\pi}, \text{ see the formula in Appendix.} \\
&= \frac{2\pi k_B T}{\omega} = \frac{2\pi}{\beta\omega}
\end{aligned} \tag{26}$$

Q.E.D.

b) According to the Equipartition of Energy theorem, what should the average energy of the system of N oscillators be?

Solution:

According to the Equipartition of Energy theorem, each quadratic term in the energy expression corresponds to one degree of freedom of the system. And each degree of freedom possesses the average energy of $\frac{1}{2}k_BT$. For the system in question, we have N particles, and the degree of freedom for each particle is 2 (since the corresponding energy expression contains two quadratic terms). So the degree of the whole system is then $2N$, which will give the average energy of the system as:

$$\langle E \rangle = 2N \times \frac{1}{2}k_BT = Nk_BT \tag{27}$$

Q.E.D.

c) Use the N-particle canonical partition function to calculate the average energy of the system and show that it agrees with your answer from the previous part.

Solution:

Here the N-particle (distinguishable) canonical partition function can be directly given based on the one-particle canonical fucntion given in a):

$$Z_N = (\frac{2\pi}{\beta\omega})^N \tag{28}$$

As for how the N-particle canonical partition function is derived from the one-particle partition function, a discussion will be given in Question-B3. Having the N-particle canonical partition function, the average energy of the system can be directly calculated:

$$\begin{aligned}\langle E\rangle &= -\frac{1}{Z_N}\cdot\frac{\partial Z_N}{\partial\beta} \\ &= -\frac{1}{(\frac{2\pi}{\beta\omega})^N}\cdot N(\frac{2\pi}{\beta\omega})^{N-1}\cdot\frac{2\pi}{\omega}\cdot\frac{-1}{\beta^2} \\ &= \frac{N}{(\frac{2\pi}{\beta\omega})^N}\cdot(\frac{2\pi}{\beta\omega})^N\cdot\frac{1}{\beta} \\ &= \frac{N}{\beta} = Nk_BT\end{aligned} \tag{29}$$

The result is identical to that from b).

Q.E.D.

d) The quantum version of this system has energies given by:

$$E_n = (n+\frac{1}{2})\hbar\omega, \text{ for } n = 0, 1, 2, 3, \cdots \tag{30}$$

Find Z_1 for this systen, and write your answer in term of a hyperbolic trigonometric function.

Solution:

The one-particle canonical partition function is given by:

$$\begin{aligned}Z_1 &= \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2}\hbar\omega)},\ \beta = \frac{1}{k_BT} \\ &= e^{-\frac{\beta\hbar\omega}{2}}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}\end{aligned} \tag{31}$$

Here the summation is again a geometric progression summation, and the formula to calculate the summation can be found in Question-A4. Here for this question, we have $a_1 = 1$ and $q = e^{-\beta\hbar\omega}$ (the two parameters for the geometric progression). Thus we have:

$$\begin{aligned}Z_1 &= e^{-\frac{\beta\hbar\omega}{2}}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} \\ &= e^{-\frac{\beta\hbar\omega}{2}}\cdot\lim_{n\to\infty}\frac{1-e^{-n\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \\ &= \frac{1}{e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}}\end{aligned} \tag{32}$$

According to the formular given in the Appendix, the one-particle canonical partition function for the quantum oscillators system can be written as:

$$Z_1 = \frac{1}{2sinh\frac{\beta\hbar\omega}{2}} \tag{33}$$

Q.E.D.

e) Calculate the average energy of the system of N quantum oscillators, and show that it reduces to the classical answer in the $\hbar \to 0$ limit.

Solution:

First, let $x = \beta\hbar\omega/2$, then we have:

$$Z_1 = \frac{1}{2sinhx} \tag{34}$$

Thus the N-particle canonical partition function is given by:

$$Z_N = (\frac{1}{2sinhx})^N \tag{35}$$

The average of the system is then:

$$\begin{aligned}
\langle E \rangle &= -\frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta} \\
&= -\frac{1}{Z_N}\frac{\partial Z_N}{\partial x}\frac{\partial x}{\partial \beta} \\
&= -\frac{1}{Z_N}\frac{\partial Z_N}{\partial x}\cdot\frac{1}{2}\hbar\omega \\
&= -(2sinhx)^N \cdot N \cdot (\frac{1}{2sinhx})^{N-1} \cdot (-\frac{1}{2}\frac{coshx}{sinh^2x}) \cdot \frac{1}{2}\hbar\omega \\
&= \frac{N\omega}{2}\frac{\hbar coshx}{sinhx}
\end{aligned} \tag{36}$$

Here it should be pointed out that the following two differentiation formula was used:

$$(sinhx)' = coshx \tag{37}$$

$$(coshx)' = sinhx \tag{38}$$

The two formula here can be easily derived considering the formula given in the Appendix (formula-5 & 6). When $\hbar \to 0$, we have $x = \beta\hbar\omega \to 0$, therefore:

$$\begin{aligned}
\langle E \rangle &= \lim_{\substack{x\to 0\\ \hbar\to 0}} \frac{N\omega}{2}\cdot\frac{\hbar}{sinhx}coshx \\
&= \frac{N\omega}{2}\lim_{\substack{x\to 0\\ \hbar\to 0}}\frac{\hbar}{sinhx}, \quad (\lim_{x\to 0} coshx = 1, \text{derivation is easy,} \\
&\qquad\qquad \text{refer to Appendix)} \\
&= \frac{N\omega}{2}\lim_{\substack{x\to 0\\ \hbar\to 0}}\frac{\partial\hbar/\partial\hbar}{\partial(sinhx)/\partial\hbar}, \quad \text{L'Hospital's rule} \\
&= \frac{N\omega}{2}\lim_{\substack{x\to 0\\ \hbar\to 0}}\frac{1}{coshx\cdot\frac{\partial x}{\partial\hbar}} \\
&= \frac{N\omega}{2}\lim_{\substack{x\to 0\\ \hbar\to 0}}\frac{1}{coshx\cdot\frac{\beta\omega}{2}} \\
&= \frac{N}{\beta}\lim_{x\to 0}\frac{1}{coshx} = \frac{N}{\beta} = Nk_BT
\end{aligned} \tag{39}$$

The result is exactly the same with the result for the classical oscillators as given in c).

Q.E.D.

f) Calculate the specific heat C for the system of quantum oscillators, and show that you recover the classical answer at small $\hbar$.

Solution:

The expression for average energy is given by (36), and again for this question, we let $x = \beta\hbar\omega/x$. Then we have the specific heat as given by:

$$\begin{aligned}
C &= \frac{\partial\langle E\rangle}{\partial T} \\
&= \frac{N\omega\hbar}{2} \cdot \left[\frac{\partial}{\partial x}\left(\frac{coshx}{sinhx}\right)\right] \cdot \frac{\partial x}{\partial T} \\
&= \frac{N\omega\hbar}{2} \cdot \left[\frac{\partial}{\partial x}\left(\frac{coshx}{sinhx}\right)\right] \cdot (-\frac{\hbar\omega}{2} \cdot \frac{1}{k_B T^2}) \\
&= \frac{N\hbar^2\omega^2}{4k_B T^2} \cdot \frac{sinh^2x - cosh^2x}{sinh^2x} \\
&= \frac{N\hbar^2\omega^2}{4k_B T} + \frac{N\omega^2}{4k_B T} \cdot \frac{\hbar^2 cosh^2x}{sinh^2x} \qquad (40)
\end{aligned}$$

When $\hbar \to 0$ (again, this means $x \to 0$), we have:

$$\begin{aligned}
C &= \lim_{\substack{x\to 0\\ \hbar\to 0}} \left(\frac{N\hbar^2\omega^2}{4k_B T} + \frac{N\omega^2}{4k_B T} \cdot \frac{\hbar^2 cosh^2x}{sinh^2x}\right) \\
&= \lim_{\hbar\to 0} \frac{N\hbar^2\omega^2}{4k_B T} + \lim_{\substack{x\to 0\\ \hbar\to 0}} \frac{N\omega^2}{4k_B T} \cdot \frac{\hbar^2 cosh^2x}{sinh^2x} \\
&= 0 + \lim_{\substack{x\to 0\\ \hbar\to 0}} \frac{N\omega^2 cosh^2x}{4k_B T} \cdot \frac{\hbar^2}{sinh^2x} \\
&= \lim_{\substack{x\to 0\\ \hbar\to 0}} \frac{N\omega^2}{4k_B T} \cdot \frac{\partial(\hbar^2)/\partial\hbar}{\partial(sinh^2x)/\partial\hbar} \\
&= \frac{N\omega^2}{4k_B T} \lim_{\substack{x\to 0\\ \hbar\to 0}} \frac{2\hbar}{2sinhxcoshx \cdot \frac{\partial x}{\partial\hbar}} \\
&= \frac{N\omega^2}{4k_B T} \lim_{\substack{x\to 0\\ \hbar\to 0}} \frac{2\hbar}{2sinhxcoshx \cdot \frac{\beta\omega}{2}} \\
&= \frac{N\omega^2}{4k_B T} \cdot \frac{1}{\beta\omega} \lim_{x\to 0} \frac{2}{(sinh^2x + cosh^2x)^2 \cdot \frac{\beta\omega}{2}} \qquad (41) \\
&= \frac{N\omega^2}{4k_B T} \cdot \frac{4}{\beta^2\omega^2} = Nk_B \qquad (42)
\end{aligned}$$

Here it should be pointed out that in step-(41), the L'Hospital's rule was used again. For classical oscillators, the average energy for the system was already given in b) - $\langle E\rangle = Nk_B T$, thus the specific heat of the classical oscillators system is $C_C = Nk_B$, which is identical to the result for quantum oscillators system, when $\hbar \to 0$.

Q.E.D.

Question-B2

a) For a gas of nonrelativistic spin-j fermions at $T = 0$, find the density of states $\Omega(E)dE$. (Here, and throughout the entirety of this question, you may neglect the electrostatic interation between ther fermions.)

Solution:

Since we have the relationship between the energy and wave vector k and also the momentum p as following:

$$E = \frac{\hbar^2 k^2}{2m} \tag{43}$$

$$E = \frac{p^2}{2m} \tag{44}$$

Thus if we can find the expression for density of states in k-space as $f(k)dk$ or in p-space as $g(p)dp$, then it should be straightforward to do the variable change either from k to E (to transfer from $f(k)dk$ to $\Omega(E)dE$) or from p to E (transfer from $g(p)dp$ to $\Omega(E)dE$). Here the exprssion for $f(k)dk$ and $g(p)dp$ is directly given as following (taking the degeneracy into consideration):

$$f(k)dk = (2j+1)\frac{Vk^2}{2\pi^2}dk \tag{45}$$

$$g(p)dp = (2j+1)\frac{4\pi V}{h^3}p^2 dp \tag{46}$$

Here we do the transformation from k to E (for p-space transformation to E, the procedure is similar) as following (keep in mind that $E = \hbar^2 k^2/2m$, thus $k = \sqrt{2mE}/\hbar$, and $dk = 1/2\cdot\sqrt{2m}/\hbar\cdot E^{-1/2}dE$):

$$\begin{aligned}
\Omega(E)dE &= (2j+1)f(k)dk \\
&= (2j+1)\frac{Vk^2}{2\pi^2}dk \\
&= (2j+1)\frac{V}{2\pi^2}\cdot\left(\frac{2mE}{\hbar^2}\right)\cdot\left(\frac{1}{2}\cdot\frac{\sqrt{2m}}{\hbar}\cdot E^{-1/2}dE\right) \\
&= 2\pi(2j+1)V\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2},\ \hbar = h/2\pi
\end{aligned} \tag{47}$$

Q.E.D.

b) For a nonrelativistic electron gas of N particles in a volume V, show that at $T = 0$ the electrons must have a maximum energy ("Fermi energy") E_F given by:

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \tag{48}$$

Solution:

When the system is at $T = 0$, it is at its ground state. Then all the electrons in the system will take up the all the energy states from low to high continously until all the electrons have been allocated the state to stay. For convenience, we talk about the question in p-space. First, the density of states in p-space is:

$$\rho_p = \frac{V}{h^3} \tag{49}$$

Basically the derivation for (49) should employ the periodic boundary condition in k-space and the relation $p = \hbar k$, the details will not be given here. Then we can imagine a 3-D sphere with the radius of p_F, where p_F is the maximum moment value for all the electrons in the system. Why 3-D sphere? That's because for each p value, actually we could have infinite number of direction in 3-D p-space. And all the possbile directions together form the sphere that we imagined. In the sphere, we have the density of states $\rho_p = \frac{V}{h^3}$, thus we should have the the total number of electrons expressed as the function of p_F (consider the two possible spin states for electron – $\pm 1/2$):

$$N = 2 \cdot \frac{V}{h^3} \cdot \frac{4}{3}\pi p_F^3 \tag{50}$$

Therefore we have:

$$\begin{aligned} p_F &= \Big(\frac{3h^3}{8\pi} \cdot \frac{N}{V}\Big)^{1/3} \\ &= (3\pi^2\hbar^3 \cdot \frac{N}{V})^{1/3} \\ &= \hbar(\frac{3\pi^2 N}{V})^{1/3} \end{aligned} \tag{51}$$

Then we have:

$$E_F = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{1/3} \tag{52}$$

Q.E.D.

c) Using the sensity of states $\Omega(E)dE$, write an integral expression for the total energy E_{tot} in this $T = 0$ Fermi system.

Solution:

Since we have the density of states expression in energy space as given in Question-a), we could then have the expression for the total electron number:

$$\begin{aligned} N &= 2\int_0^{E_F} \Omega(E)dE, \text{ factor 2 for spin states} \\ &= 2(2\pi V)(\frac{2m}{h^2})^{3/2} \int_0^{E_F} E^{1/2}dE \\ &= \frac{8\pi V}{3}(\frac{2m}{h^2})^{3/2} E_F^{3/2} \end{aligned} \tag{53}$$

Since the density of states is given as:

$$\Omega(E) = 2\pi(\frac{2m}{h^2})^{3/2} E^{1/2} \tag{54}$$

By simply deviding (53) by (54), we have:

$$\Omega(E) = \frac{3}{4}\frac{N}{E_F}(\frac{E}{E_F})^{1/2} \tag{55}$$

Then the total energy of the Fermi system is:

$$\begin{aligned} E_{tot} &= \int_0^{E_F} 2\Omega(E) \cdot E \cdot dE \\ &= 2\int_0^{E_F} E \cdot \frac{3}{4} \cdot \frac{N}{E_F}(\frac{E}{E_F})^{1/2} dE \\ &= \frac{3N}{2E_F^{3/2}} \int_0^{E_F} E^{3/2}dE \end{aligned} \tag{56}$$

Q.E.D.

d) Show that the total energy in the system is given by:

$$E_{tot} = \frac{3}{5}NE_F \tag{57}$$

Solution:

Calculate the integral given by (56) will give us:

$$\begin{aligned} E_{tot} &= \frac{3N}{2E_F^{3/2}} \cdot \Big(\frac{2}{5}E^{5/2}\Big|_0^{E_F}\Big) \\ &= \frac{3}{5}NE_F \end{aligned} \tag{58}$$

Q.E.D.

e) Using the First Law of Thermadynamics, write an expression for the pressure as an appropriate derivative of the energy. Make sure to indicate which parameters are being held constant!

Solution:

Considering the mathematical expression for thermodynamics first law corresponding to the open system:

$$dE = TdS - PdV + \mu dN \tag{59}$$

And specifically for this question we have $T = 0$ (see the question body), thus we have:

$$dE = -PdV + \mu dN \tag{60}$$

Then obviously we have:

$$P = (\frac{dE}{dV})_N \tag{61}$$

Q.E.D.

f) Use your expression from the previous part to show that the $T = 0$ electron gas has a pressure given by:

$$p = \frac{2NE_F}{5V} \tag{62}$$

Solution:

We have the total energy of the system E_{tot} expressed as a function of N and E_F given by d) and b):

$$E_{tot} = \frac{3}{5}NE_F = \frac{3}{5}N\frac{\hbar^2}{2m}(3\pi^2N)^{2/3}V^{-2/3} \tag{63}$$

Then following the answer from e), we should have:

$$\begin{aligned} P &= -\frac{dE_{tot}}{dV} \\ &= -\frac{3}{5}N\frac{\hbar^2}{2m}(3\pi^2N)^{2/3}(-\frac{2}{3}V^{-2/3}V^{-1}) \\ &= \frac{2}{5}\Big[\frac{\hbar^2}{2m}(\frac{3\pi^2N}{V})^{2/3}\Big]V^{-1} \\ &= \frac{2NE_F}{V} \end{aligned} \tag{64}$$

Q.E.D.

Question-B3

a) Consider a monatomic ideal gas of N classical but indistinguishable particles in a box of Volume V, with chemical potential μ, at temperature T. What is the N-particle canonical partition function for this system?

Solution:

First of all, for the N indistinguishable particles system, the N-particle canonical partition function is given by:

$$Z_N = \frac{1}{N!}[Z_1(T,V)]^N = \frac{1}{N!}\Big(\sum_s e^{-\beta\epsilon_s}\Big)^N \tag{65}$$

where Z_1 is the one-particle canonical partition function of the system. As for how the N-particle canonical partition function of the system is derived, refer to the Appendix.

To calculate (65), we should recall the relation between energy ϵ_s and the momentum p: $\epsilon_s = p^2/2m$, and the number of p value within the range $p \to p + dp$ is already given in Question-B2 (46):

$$g(p)dp = \frac{4\pi V}{h^3}p^2 dp \tag{66}$$

Therefore the summation in (65) can be turned into an integral as following:

$$\begin{aligned} Z_N &= \frac{1}{N!}\Big(\sum_s e^{-\beta\epsilon_s}\Big)^N \\ &= \frac{1}{N!}\Big[\int_0^\infty e^{-\beta\epsilon_s} g(p)dp\Big]^N \\ &= \frac{1}{N!}\Big[\int_0^\infty \frac{4\pi V p^2 e^{-\beta p^2/2m} dp}{h^3}\Big]^N \\ &= \frac{1}{N!}\Big[\frac{4\pi V}{h^3}\int_0^\infty p^2 e^{-\beta p^2/2m} dp\Big]^N \end{aligned} \tag{67}$$

To calculate the integral in the last step of (67), let's consider the following integral (which is given in the Appendix):

$$\begin{aligned} \int_0^\infty e^{-ax^2}dx &= xe^{-ax^2}\Big|_0^\infty - \int_0^\infty x(-2ax)e^{-ax^2}dx \\ &= 2a\int_0^\infty x^2 e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}} \\ &\Longrightarrow \\ \int_0^\infty x^2 e^{-ax^2}dx &= \frac{1}{4a}\sqrt{\frac{\pi}{a}} \end{aligned} \tag{68}$$

Thus we can calculate the integral in (67) to obtain the N-particle canonical partition function of the system:

$$\begin{aligned} Z_N &= \frac{1}{N!}\Big[\frac{4\pi V}{h^3}\frac{m}{2\beta}\sqrt{\frac{\pi}{\beta/2m}}\Big]^N \\ &= \frac{V^N}{N!}\Big(\frac{2\pi m k_B T}{h^2}\Big)^{3N/2} \end{aligned} \tag{69}$$

Q.E.D.

b) Define the thermal de Broglie wavelength λ for this system, and express your answer to the previous part in terms of $N, V,$ and λ.

Solution:

First of all we have:

$$\lambda = \frac{h}{p} \tag{70}$$
$$E_k = \frac{p^2}{2m} \tag{71}$$

Thus we have:

$$\lambda = \frac{h}{\sqrt{2mE_k}} \tag{72}$$

The effective kinetic energy of free particles is given as $E_k = \pi k_B T$, which can be derived considering the Maxwell-Boltzmann distribution:

$$\begin{aligned} f(v)dv &= \sqrt{\left(\frac{m}{2\pi k_B T}\right)^3} 4\pi v^2 e^{-\frac{mv^2}{2k_B T}} dv \\ &\Longrightarrow \\ E_k &= \int_0^\infty \frac{1}{2} m v^2 f(v) dv = \pi k_B T \end{aligned} \tag{73}$$

Here the integral calculation again will need the same trick as used in a), and the specific steps will not be given here due to its tedious calculation. Thus we have the expression for the thermal de Broglie wavelength:

$$\begin{aligned} \lambda &= \frac{h}{\sqrt{2mE_k}} \\ &= \frac{h}{\sqrt{2\pi m k_B T}} \\ &= \left(\frac{\beta h^2}{2\pi m}\right)^{1/2}, \ \beta = \frac{1}{k_B T} \end{aligned} \tag{74}$$

The N-particle partition energy is given as (see a)):

$$\begin{aligned} Z_N &= \frac{V^N}{N!} \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \\ &= \frac{1}{N!} \left[\frac{V}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2}\right]^N \\ &= \frac{1}{N!} \left[V \left(\frac{2\pi m}{\beta h^2}\right)^{3/2}\right]^N \end{aligned} \tag{75}$$

Considering the expresstion for the thermal de Broglie wavelength (74), we have:

$$Z_N = \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N \tag{76}$$

Q.E.D.

c) Using your answer for the canonical partition function, find the average energy $\langle E \rangle$ of the gas and state how your answer agrees with the Equipartition of Energy theorem.

Solution:

The average energy $\langle E\rangle$ can be directly calculated given the N-particle partition function:

$$\begin{aligned}
\langle E\rangle &= -\frac{1}{Z_N}\frac{\partial Z_N}{\partial\beta} \\
&= -\frac{1}{Z_N}\frac{\partial Z_N}{-\frac{1}{k_BT^2}\partial T} \\
&= \frac{k_BT^2}{\frac{V^N}{N!}\left(\frac{2\pi mk_BT}{h^2}\right)^{3N/2}}\frac{V^N}{N!}\cdot\frac{3}{2}N\cdot\left(\frac{2\pi mk_BT}{h^2}\right)^{\frac{3}{2}N-1}\cdot\frac{2\pi mk_B}{h^2} \\
&= \frac{k_BT^2}{\frac{V^N}{N!}\left(\frac{2\pi mk_BT}{h^2}\right)^{3N/2}}\frac{V^N}{N!}\cdot\frac{3}{2}N\cdot\left(\frac{2\pi mk_BT}{h^2}\right)^{\frac{3}{2}N}\cdot\frac{1}{T} \\
&= \frac{3}{2}Nk_BT
\end{aligned} \tag{77}$$

According to the Equipartition of Energy theorem, each degree of freedom possesses the averave energy of $1/2k_BT$, since we have N particles in the system and the degree of freedom for each particle is 3 (because we need 3 coordinates to describe where the particle is in 3-D space), thus the total degree of freedom of the system is $3N$. Then the average energy is directly given as $3N\times 1/2k_BT = 3/2k_BT$, which is identical to the result we obtain from the canonical partition energy.

Q.E.D.

d) Show that the grand partition function of this system is given by

$$\mathcal{Z} = exp(e^{\beta\mu}\frac{V}{\lambda^3}) \tag{78}$$

Solution:

The grand partition function is given by:

$$\begin{aligned}
\mathcal{Z}(\mu,V,T) &= \sum_i e^{(N_i\mu-E_i)/k_BT},\ \text{definition} \\
&= \sum_{N_i} e^{N_i\frac{\mu}{k_BT}}\cdot\sum_{i(N=N_i)} e^{-\frac{E_i}{k_BT}} \\
&= \sum_{N_i} e^{N_i\frac{\mu}{k_BT}}\cdot Z_{N_i}(V,T)
\end{aligned} \tag{79}$$

Considering the N-particle canonical partition function of the system given in (b)):

$$Z_N = \frac{1}{N!}(\frac{V}{\lambda^3})^N \tag{80}$$

we then have:

$$\begin{aligned}
\mathcal{Z}(\mu,V,T) &= \sum_{N_i}(e^{\beta\mu})^{N_i}\cdot\frac{1}{N_i!}\cdot(\frac{V}{\lambda^3})^{N_i} \\
&= \sum_{N_i}\frac{1}{N_i!}\left(\frac{e^{\beta\mu}V}{\lambda^3}\right)^{N_i} = exp(e^{\beta\mu}\frac{V}{\lambda^3})
\end{aligned} \tag{81}$$

Here it should be noticed that (81) is just the Taylor expansion.

Q.E.D.

e) In the grand canonical ensemble, find the average number of particles $\langle N\rangle$ in this system.

Solution:

First define $\Gamma \equiv e^{\beta\mu}$, then $\mathcal{Z} = e^{\Gamma \frac{V}{\lambda^3}}$, then the average particle number $\langle N \rangle$ is given by:

$$\begin{aligned}\langle N \rangle &= \Gamma \frac{\partial}{\partial \Gamma} ln\mathcal{Z} \\ &= \Gamma \frac{1}{\mathcal{Z}} \frac{V}{\lambda^3} e^{\Gamma \frac{V}{\lambda^3}} \\ &= \frac{\Gamma V}{\lambda^3}\end{aligned} \tag{82}$$

Q.E.D.

f) From the grand partition function, find an expression for the average pressure P, and show that when combined with the previous answer, it implies the equation of state $PV = \langle N \rangle k_B T$.

Solution:

First of all, we have the expression for Helmholtz free energy as:

$$A = -k_B T ln\mathcal{Z} \tag{83}$$

Also we know that the reduction of the Helmholtz free energy of the system equals to the work done by the system to the surroundings through the change of volume only. Thus at pressure P, we should have:

$$A_{initial} - A_{final} = P(V_{final} - V_{initial}) \tag{84}$$

The *l.f.s.* is the reduction of the Helmholtz free energy, and the *r.h.s.* is the work done by the system to the surroundings through volume expansion. Combining (83) and (84), we should have:

$$PV = k_B T ln\mathcal{Z} \tag{85}$$

Then we have the expression for the average pressure P:

$$\begin{aligned}P &= \frac{k_B T}{V} ln\mathcal{Z} \\ &= \frac{k_B T}{V} ln(e^{\Gamma \frac{V}{\lambda^3}}) \\ &= \frac{k_B T \Gamma}{\lambda^3}\end{aligned} \tag{86}$$

Then considering the expression for average particle number $\langle N \rangle$ given in e), we have:

$$\frac{PV}{k_B T} = \frac{\frac{k_B T \Gamma}{\lambda^3} V}{k_B T} = \frac{\Gamma V}{\lambda^3} = \langle N \rangle \tag{87}$$

Thus we have the equation of state for the system:

$$PV = \langle N \rangle k_B T \tag{88}$$

Q.E.D.

Question-B4

a) Consider a system of N distinguishable spin-1 magnetic dipoles in an external magnetic filed $\vec{H} = H\vec{z}$. Recall that the energy of a magnetic dipole with magnetic moment $\vec{\mu}$ in a magnetic filed $\vec{H}$ is given by $E = -\vec{\mu}\cdot\vec{H}$, and the magnetic moments are quantized such that $\mu_z = g\mu_B m_l$ for an appropriate set of numbers m_l. (In this problem you may neglect the kinetic energy of the dipoles) What are the allowed values of m_l?

Solution:

Since we have the spin-1 magnetic dipoles, the projection of spin of the magentic dipole on z-axis can be $0, \pm 1$, thus the allowed value of m_l is $0, \pm 1$, i.e. $m_l = 0, \pm 1$.

Q.E.D.

b) Show that the N-particle partition function of this system is:

$$Z_N = (1 + 2coshx)^N \tag{89}$$

where $x \equiv \beta g \mu_B H$.

Solution:

Here in this question, we have distinguishable partilces in the system, thus we don't need to consider the overcounting of states. The N-particle partition function is given by:

$$Z_N = (Z_1)^N \tag{90}$$

First of all, the one-particle partition function is given as:

$$Z_1 = \sum_s e^{-\epsilon_s \beta} \tag{91}$$

where s refers to the state for which $m_l = 0, \pm 1$, in this question. Considering energy expression given in the question $E = -\vec{\mu}\cdot\vec{H}$, we have:

$$\begin{aligned} Z_1 &= \underbrace{1}_{m_l=0} + \underbrace{e^{-\beta g \mu_B H}}_{m_l=-1} + \underbrace{e^{\beta g \mu_B H}}_{m_l=+1} \\ &= 1 + 2coshx \end{aligned} \tag{92}$$

Then we have the N-particle partition function given by:

$$Z_N = (1 + 2coshx)^N \tag{93}$$

Q.E.D.

c) Find the average energy of this system as a function of x, and describe why your answer makes sense in hte $T = 0$ and $T \to \infty$ limits.

Solution:

The average energy of the system is given by:

$$\begin{aligned} \langle E \rangle &= -\frac{1}{Z_N}\frac{\partial Z_N}{\partial \beta} \\ &= -\frac{1}{Z_N}\frac{\partial Z_N}{\partial x}\frac{\partial x}{\partial \beta} \\ &= -\frac{N}{(1+2coshx)^N}\cdot(1+2coshx)^{N-1}\cdot 2sinhx\cdot(g\mu_B H) \\ &= \frac{-2Ng\mu_B H sinhx}{1+2coshx} \\ &= -Ng\mu_B H\frac{e^x - e^{-x}}{e^x + e^{-x} + 1} \end{aligned} \tag{94}$$

Furthermore, when $T = 0$, we have $x \to \infty$, thus:

$$\begin{aligned}
\langle E \rangle &= \lim_{x\to\infty} \Big(-Ng\mu_B H \frac{e^x - e^{-x}}{e^x + e^{-x} + 1} \Big) \\
&= \lim_{x\to\infty} \Big(-Ng\mu_B H \frac{e^x + e^{-x}}{e^x - e^{-x}} \Big), \text{ L'Hospital's rule} \\
&= \lim_{x\to\infty} \Big(-Ng\mu_B H \frac{1 + e^{-2x}}{1 - e^{-2x}} \Big) \\
&= -Ng\mu_B H
\end{aligned} \tag{95}$$

which makes sense since when $T = 0$, all the magnetic dipoles are aligned along the direction of the external magnetic filed $\vec{H}$, leading to the average energy of the system given by $\langle E \rangle = -(Ng\mu_B)H$. This is exactly the same with the result given by (95).
When $T \to \infty$, we have $x = 0$, thus:

$$\begin{aligned}
\langle E \rangle &= \lim_{x\to 0} \Big(-Ng\mu_B H \frac{e^x - e^{-x}}{1 + e^x + e^{-x}} \Big) \\
&= 0
\end{aligned} \tag{96}$$

which also makes sense since when the temperature goes to infinity, all the magnetic dipoles will be oriented randomly rather than aligned up by the external magnetic field. This will give the net magnetic moment 0, thus the average energy is 0.

Q.E.D.

d) Give an expression for the average magnetization M of this system as a derivative of the partition function.

Solution:

For one-partilce, we have the average magnetization given by:

$$\begin{aligned}
M &= \frac{\underbrace{0}_{m_l=0} + \underbrace{g\mu_B e^{\beta g\mu_B H}}_{m_l=1} + \underbrace{(-g\mu_B e^{-\beta g\mu_B H})}_{m_l=-1}}{Z_1} \\
&= \frac{g\mu_B (e^{\beta g\mu_B H} - e^{-\beta g\mu_B H})}{Z_1}
\end{aligned} \tag{97}$$

The one-particle canonical partition function is given in b) as:

$$Z_1 = 1 + e^{\beta g\mu_B H} - e^{-\beta g\mu_B H} \tag{98}$$

Thus we have:

$$\begin{aligned}
\frac{\partial Z_1}{\partial H} &= -g\mu_B \beta e^{-\beta g\mu_B H} + g\mu_B \beta e^{\beta g\mu_B H} \\
&= g\mu_B \beta (e^{\beta g\mu_B H} - e^{-\beta g\mu_B H})
\end{aligned} \tag{99}$$

By comparing (97) and (99), we have:

$$M = \frac{1}{\beta Z_1} \frac{\partial Z_1}{\partial H} \tag{100}$$

Generally for N-particle system, we have similar expression:

$$M = \frac{1}{\beta Z_N} \frac{\partial Z_N}{\partial H} \tag{101}$$

Q.E.D.

e) Find the average magnetization M of this system as a function of x, and describe why your answer makes sense at $T = 0$ and $T \to \infty$ limits.

Solution:

By comparing the expression for average energy $\langle E \rangle$ given in c) and the average magnetization expression M given in d), we have:

$$\begin{aligned} M &= -\frac{\langle E \rangle}{H} \\ &= Ng\mu_B \frac{e^x - e^{-x}}{e^x + e^{-x} + 1} \end{aligned} \tag{102}$$

Again we have when $T = 0$, $x \to \infty$ and when $T \to \infty$, $x = 0$. By carrying out similar limit calculation as given in (95) and (96), we have:

$$T = 0 \Longrightarrow M = Ng\mu_B \tag{103}$$

$$T \to \infty \Longrightarrow M = 0 \tag{104}$$

Again, the result given here makes sense: for $T = 0$, all the magnetic dipoles are aligned along the external magnetic field giving the average magnetization of $Ng\mu_B$; for $T \to \infty$, all the magnetic dipoles orients randomly giving the average magnetization of 0.

Q.E.D.

f) Find the magnetic susceptibility

$$\chi \equiv \lim_{H \to 0} \left(\frac{\partial M}{\partial H} \right)_T \tag{105}$$

and show that the Curie constant $C \equiv \chi T$ is given by:

$$C = \frac{2N}{3k_B} (g\mu_B)^2 \tag{106}$$

Solution:

First of all, the average magnetization M is given as:

$$M = Ng\mu_B \frac{e^x - e^{-x}}{e^x + e^{-x} + 1} \tag{107}$$

Then we have:

$$\begin{aligned} \left(\frac{\partial M}{\partial H} \right)_T &= \left(\frac{\partial M}{\partial x} \cdot \frac{\partial x}{\partial H} \right)_T \\ &= Ng\mu_B \\ &\quad \times \frac{(e^x + e^{-x})(e^x + e^{-x} + 1) - (e^x - e^{-x})(e^x - e^{-x})}{(e^x + e^{-x} + 1)^2} \\ &\quad \times (\beta g\mu_B) \\ &= N\beta (g\mu_B)^2 \frac{4 + e^x + e^{-x}}{(e^x + e^{-x} + 1)^2} \end{aligned} \tag{108}$$

When $H \to 0$, we have $x = \beta g\mu_B H \to 0$, thus we have the magnetic susceptibility of the system given by:

$$\begin{aligned} \chi &\equiv \lim_{x \to 0} \left(\frac{\partial M}{\partial H} \right)_T \\ &= \lim_{x \to 0} \left[N\beta (g\mu_B)^2 \frac{4 + e^x + e^{-x}}{(e^x + e^{-x} + 1)^2} \right] \\ &= \frac{2N}{3k_B T} (g\mu_B)^2, \ \beta = \frac{1}{k_B T} \end{aligned} \tag{109}$$

Then natually we have the Curie constant C given by:

$$\begin{aligned} C \equiv \chi T &= \frac{2N}{3k_B T}(g\mu_B)^2 \cdot T \\ &= \frac{2N}{3k_B}(g\mu_B)^2 \end{aligned} \tag{110}$$

Q.E.D.

Question-B5

In the Grand Canonical Ensemble, calculate the fluctuations $\langle(\Delta E)^2\rangle$, $\langle(\Delta N)^2\rangle$ and $\langle\Delta N\Delta E\rangle$ in terms of appropriate derivatives of the average values of E and N with respect to the chemical potential μ and the temperature T. Be sure to indicate in detail what quantities are held fixed. Recall that $\Delta X = X - \langle X\rangle$ for any quantity X.

Solution:

Given the definition for the grand partition function:

$$\mathcal{Z}(z,V,T) = \sum_{N_i} z^{N_i} Z(N_i,V,T) \tag{111}$$

where $z \equiv exp(\mu/k_BT)$ and $Z(N_i,V,T)$ is the canonical partition function corresponding to particle number N_i, we can do the following calculation:

$$\begin{aligned}
\frac{\partial[\mathcal{Z}(z,V,T)]}{\partial\mu} &= \sum_{N_i}(N_i z^{N_i-1})(\frac{\partial z}{\partial \mu})Z(N_i,V,T) \\
&= \sum_{N_i}(N_i z^{N_i-1})(\beta e^{\mu/k_BT})Z(N_i,V,T),\ \beta = 1/k_BT \\
&= \beta\sum_{N_i} N_i z^{N_i} Z(N_i,V,T) \\
&= \beta\mathcal{Z}\cdot\frac{\sum_{N_i} N_i z^{N_i} Z(N_i,V,T)}{\mathcal{Z}} \\
&= \beta\mathcal{Z}\langle N\rangle
\end{aligned} \tag{112}$$

Then we have:

$$\begin{aligned}
\langle N\rangle &= \frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial[\mathcal{Z}(z,V,T)]}{\partial\mu} \\
&= \frac{1}{\beta}\frac{\partial\{ln[\mathcal{Z}(z,V,T)]\}}{\partial\mu}
\end{aligned} \tag{113}$$

Similar we can also calculate:

$$\begin{aligned}
\frac{\partial\mathcal{Z}(z,V,T)}{\partial\beta} &= \sum_{N_i}\big[(N_i z^{N_i-1})(\frac{\partial z}{\partial\beta})Z(N_i,V,T) \\
&\qquad + z^{N_i}\frac{\partial[Z(N_i,V,T)]}{\partial\beta}\big] \\
&= \sum_{N_i}\big[\mu N_i z^{N_i}Z(N_i,V,T) - E_i z^{N_i}Z(N_i,V,T)\big] \\
&= \mu\mathcal{Z}\langle N\rangle - E\mathcal{Z}
\end{aligned} \tag{114}$$

Then we have:

$$\begin{aligned}
\langle E\rangle &= -\frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\beta} + \mu\langle N\rangle \\
&= -\frac{\partial ln\mathcal{Z}}{\partial\beta} + \mu\langle N\rangle
\end{aligned} \tag{115}$$

To calculate the energy and particle number fluctuations, we need the following relations:

$$\begin{aligned}
\langle(\Delta X)^2\rangle &= \langle(X-\langle X\rangle)^2\rangle \\
&= \langle X^2 - 2\langle X\rangle X + \langle X\rangle^2\rangle \\
&= \langle X^2\rangle - 2\langle X\rangle\langle X\rangle + \langle X\rangle^2 \\
&= \langle X^2\rangle - \langle X\rangle^2
\end{aligned} \tag{116}$$

where X is any observable for the system, thus by replacing X with either N - particle number or E - energy, we have:

$$\langle(\Delta N)^2\rangle = \langle N^2\rangle - \langle N\rangle^2 \tag{117}$$

$$\langle(\Delta E)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 \tag{118}$$

As for $\langle\Delta N\Delta E\rangle$, we have:

$$\begin{aligned}\langle\Delta N\Delta E\rangle &= \langle[N-\langle N\rangle]\rangle\langle[E-\langle E\rangle]\rangle \\ &= \langle NE - \langle N\rangle E - N\langle E\rangle + \langle N\rangle\langle E\rangle\rangle \\ &= \langle NE\rangle - \langle N\rangle\langle E\rangle - \langle E\rangle\langle N\rangle + \langle N\rangle\langle E\rangle \\ &= \langle NE\rangle - \langle N\rangle\langle E\rangle \end{aligned} \tag{119}$$

Then to calculate $\langle(\Delta N)^2\rangle$, we start from the following calculation (refer to expression-(113)):

$$\begin{aligned}\frac{\partial\langle N\rangle}{\partial\mu} &= \frac{1}{\beta}\frac{\partial^2 ln\big[\mathcal{Z}(\mu,V,T)\big]}{\partial\mu^2} \\ &= \frac{1}{\beta}\frac{\partial}{\partial\mu}\big(\frac{1}{\mathcal{Z}}\cdot\frac{\partial\mathcal{Z}}{\partial\mu}\big) \\ &= \frac{1}{\beta}\big[\frac{1}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\mu^2} - \frac{1}{\mathcal{Z}^2}\big(\frac{\partial\mathcal{Z}}{\partial\mu}\big)^2\big]\end{aligned} \tag{120}$$

For the first term of (120), we have:

$$\begin{aligned}\frac{\partial\mathcal{Z}(z,V,T)}{\partial\mu} &= \frac{\sum_{N_i} z^{N_i}Z(N_i,V,T)}{\partial z}\cdot\frac{\partial z}{\partial\mu} \\ &= \sum_{N_i} N_i z^{N_i-1}Z(N_i,V,T)\cdot\beta z \\ &= \beta\sum_{N_i} z^{N_i}Z(N_i,V,T)\end{aligned} \tag{121}$$

Continuing the similar calculation as shown in (121), we have:

$$\begin{aligned}\frac{\partial^2\mathcal{Z}}{\partial\mu^2} &= \beta^2\sum_{N_i} N_i^2 z^{N_i}Z(N_i,V,T) \\ &= \beta^2\mathcal{Z}\langle N^2\rangle\end{aligned} \tag{122}$$

Then we know the first term in (120) is $\beta\langle N^2\rangle$. As for the second term, it is straightforward to see that it is actually $\beta\langle N\rangle^2$ considering (113). Thus we have:

$$\begin{aligned}\frac{\partial\langle N\rangle}{\partial\mu} &= \beta[\langle N^2\rangle - \langle N\rangle^2] \\ &= \beta\langle(\Delta N)^2\rangle \\ &\Rightarrow \\ \langle(\Delta N)^2\rangle &= k_B T\big(\frac{\partial\langle N\rangle}{\partial\mu}\big)_{T,V}\end{aligned} \tag{123}$$

This is the expression for particle number fluctuation, where the temperature – T and volume – V are kept as constant.
Then we calculate $\langle\Delta N\Delta E\rangle$, to do this, we start from the following expression (see (114)):

$$\frac{\partial\mathcal{Z}(z,V,T)}{\partial\beta} = \sum_{N_i}\big[-E_i z^{N_i}Z(N_i,V,T) + \mu N_i z^{N_i}Z(N_i,V,T)\big] \tag{124}$$

Then we have:

$$\begin{aligned}\frac{\partial}{\partial\mu}(\frac{\partial\mathcal{Z}}{\partial\beta}) &= \sum_{N_i}\big[-\beta E_i N_i z^{N_i} Z(N_i,V,T) \\ &\quad + N_i z^{N_i} Z(N_i,V,T) + \beta\mu N_i^2 z^{N_i} Z(N_i,V,T)\big] \\ &= -\beta\mathcal{Z}\langle NE\rangle + \mathcal{Z}\langle N\rangle + \beta\mu\mathcal{Z}\langle N^2\rangle \end{aligned} \tag{125}$$

Thus we have:

$$\langle NE\rangle = -\frac{1}{\beta\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta\partial\mu} + \frac{1}{\beta}\langle N\rangle + \mu\langle N^2\rangle \tag{126}$$

Considering the expression for $\langle E\rangle$ – (115) and $\langle N\rangle$ – (113), we have:

$$\langle E\rangle\langle N\rangle = -\frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\beta}(\frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\mu}) + \mu\langle N\rangle^2 \tag{127}$$

Therefore we have:

$$\begin{aligned}\langle\Delta N\Delta E\rangle &= \langle NE\rangle - \langle N\rangle\langle E\rangle \\ &= -\frac{1}{\beta\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta\partial\mu} + \frac{1}{\beta}\langle N\rangle + \frac{1}{\beta\mathcal{Z}}(\frac{\partial\mathcal{Z}}{\partial\beta})(\frac{\partial\mathcal{Z}}{\partial\mu}) \\ &\quad + \mu(\langle N^2\rangle - \langle N\rangle^2) \\ &= \frac{1}{\beta}\big[-\frac{1}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta\partial\mu} + \frac{1}{\mathcal{Z}^2}(\frac{\partial\mathcal{Z}}{\partial\beta})(\frac{\partial\mathcal{Z}}{\partial\mu}) + \langle N\rangle\big] + \mu\langle(\Delta N)^2\rangle \\ &= \frac{1}{\beta}\frac{\partial\langle E\rangle}{\partial\mu} + \mu\langle(\Delta N)^2\rangle \end{aligned} \tag{128}$$

Here to get (128), we utilize the following identity:

$$\begin{aligned}\frac{\partial\langle E\rangle}{\partial\beta} &= \frac{\big[-\frac{\partial ln\mathcal{Z}}{\partial\beta} + \mu\langle N\rangle\big]}{\partial\mu} \\ &= -\frac{1}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta\partial\mu} + \frac{1}{\mathcal{Z}^2}(\frac{\partial\mathcal{Z}}{\partial\beta})(\frac{\partial\mathcal{Z}}{\partial\mu}) + \langle N\rangle \end{aligned} \tag{129}$$

Based on (128), we have:

$$\langle\Delta N\Delta E\rangle = \frac{1}{\beta}(\frac{\partial\langle E\rangle}{\partial\mu})_{T,V} + \frac{\mu}{\beta}(\frac{\partial\langle N\rangle}{\partial\mu})_{T,V} \tag{130}$$

Here the temperature – T and the volume – V, are kept as constant. To calculate $\langle(\Delta E)^2\rangle$, we again start from (124):

$$\frac{\partial\mathcal{Z}(z,V,T)}{\partial\beta} = \sum_{N_i}\left[-E_i z^{N_i} Z(N_i,V,T) + \mu N_i z^{N_i} Z(N_i,V,T)\right] \tag{131}$$

We then have:

$$\begin{aligned}\frac{\partial^2\mathcal{Z}(z,V,T)}{\partial\beta^2} &= \sum_{N_i}\big[E_i^2 z^{N_i} Z(N_i,V,T) - \mu E_i N_i z^{N_i} Z(N_i,V,T) \\ &\quad + \mu^2 N_i^2 z^{N_i} Z(N_i,V,T) \\ &\quad - \mu E_i N_i z^{N_i} Z(N_i,V,T) \\ &= \mathcal{Z}\langle E^2\rangle - 2\mu\mathcal{Z}\langle NE\rangle + \mathcal{Z}\mu^2\langle N\rangle^2 \end{aligned} \tag{132}$$

Thus we have the expression for $\langle E^2\rangle$:

$$\langle E^2\rangle = \frac{1}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta^2} + 2\mu\langle NE\rangle - \mu^2\langle N^2\rangle \tag{133}$$

From (115), we know:

$$\langle E\rangle = -\frac{\partial ln\mathcal{Z}}{\partial\beta} + \mu\langle N\rangle \tag{134}$$

Thus we have:

$$\begin{aligned}\langle E\rangle^2 &= (\mu\langle N\rangle - \frac{1}{\mathcal{Z}}\frac{\partial Z}{\partial\beta})^2\\ &= \mu^2\langle N\rangle^2 - \frac{2\mu}{\mathcal{Z}}\langle N\rangle\frac{\partial\mathcal{Z}}{\partial\beta} + \frac{1}{\mathcal{Z}^2}(\frac{\partial\mathcal{Z}}{\partial\beta})^2\end{aligned} \tag{135}$$

Therefore:

$$\begin{aligned}\langle(\Delta E)^2\rangle &= \langle E^2\rangle - \langle E\rangle^2\\ &= \big[\frac{1}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta^2} + 2\mu\langle NE\rangle - \mu^2\langle N^2\rangle\big]\\ &\quad - \big[\mu^2\langle N\rangle^2 - \frac{2\mu}{\mathcal{Z}}\langle N\rangle\frac{\partial\mathcal{Z}}{\partial\beta} + \frac{1}{\mathcal{Z}^2}(\frac{\partial\mathcal{Z}}{\partial\beta})^2\big],\ \big[(126) \to \langle NE\rangle\big]\\ &= \big[\frac{1}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta^2} + 2\big(-\frac{1}{\beta\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta\partial\mu} + \frac{1}{\beta}\langle N\rangle + \mu\langle N^2\rangle\big) - \mu^2\langle N^2\rangle\big]\\ &\quad - \big[\mu^2\langle N\rangle^2 - \frac{2\mu}{\mathcal{Z}}\langle N\rangle\frac{\partial\mathcal{Z}}{\partial\beta} + \frac{1}{\mathcal{Z}^2}(\frac{\partial\mathcal{Z}}{\partial\beta})^2\big]\\ &= \big[\frac{1}{\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta^2} - \frac{1}{\mathcal{Z}}(\frac{\partial\mathcal{Z}}{\partial\beta})^2\big] + \mu^2\big[\langle N^2\rangle - \langle N\rangle^2\big]\\ &\quad + \big[-\frac{2\mu}{\beta\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta\partial\mu} + \frac{2\mu}{\beta}\langle N\rangle + \frac{2\mu}{\mathcal{Z}}\langle N\rangle\frac{\partial\mathcal{Z}}{\partial\beta}\big]\\ &= \frac{\partial\big(\frac{1}{\mathcal{Z}}\cdot\frac{\partial\mathcal{Z}}{\partial\beta}\big)}{\partial\beta} + \mu^2\langle(\Delta N)^2\rangle\\ &\quad + \big[-\frac{2\mu}{\beta\mathcal{Z}}\frac{\partial^2\mathcal{Z}}{\partial\beta\partial\mu} + \frac{2\mu}{\beta^2\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\mu} + \frac{2\mu}{\mathcal{Z}^2\beta}\frac{\partial\mathcal{Z}}{\partial\mu}\frac{\partial\mathcal{Z}}{\partial\beta}\big]\\ &= \frac{\partial\big(\frac{1}{\mathcal{Z}}\cdot\frac{\partial\mathcal{Z}}{\partial\beta}\big)}{\partial\beta} + \frac{\mu^2}{\beta}\cdot\frac{\partial\langle N\rangle}{\partial\mu} + \big[-2\mu\frac{\partial\big(\frac{1}{\beta}\cdot\frac{1}{\mathcal{Z}}\cdot\frac{\partial\mathcal{Z}}{\partial\mu}\big)}{\partial\beta}\big]\\ &= \frac{\partial\big(\mu\langle N\rangle - \langle E\rangle\big)}{\partial\beta} + \frac{\mu^2}{\beta}\cdot\frac{\partial\langle N\rangle}{\partial\mu} - 2\mu\frac{\partial\langle N\rangle}{\partial\beta}\\ &= \frac{\mu^2}{\beta}\cdot(\frac{\partial\langle N\rangle}{\partial\mu})_{V,T} - (\frac{\partial\langle E\rangle}{\partial\beta})_{V,T} - (\mu\frac{\partial\langle N\rangle}{\partial\beta})_{V,T}\end{aligned} \tag{136}$$

This is the expressioon for fluctuation $\langle\Delta N\Delta E\rangle$, where the temperature – T and volume – V is kept as constant.

Q.E.D.

Appendices

Useful Formula

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}}, \text{ for } Re(a) > 0. \tag{137}$$

$$sinhx \approx x + \frac{x^3}{3!} + \cdots \tag{138}$$

$$coshx \approx 1 + \frac{x^2}{2!} + \cdots \tag{139}$$

$$e^x = \sum_0^{\infty} \frac{x^n}{n!} \tag{140}$$

$$sinhx = \frac{e^x - e^{-x}}{2} \tag{141}$$

$$coshx = \frac{e^x + e^{-x}}{2} \tag{142}$$

The N-particles system

For any given N-particle system, the N-particle canonical partition function is given by:

$$Z_N = \left(\sum_{s_1} e^{-\beta\epsilon_{s_1}}\right) \cdot \left(\sum_{s_2} e^{-\beta\epsilon_{s_2}}\right) \cdot \cdots \cdot \left(\sum_{s_N} e^{-\beta\epsilon_{s_N}}\right) \tag{143}$$

However there is still a problem, for indistinguishable particles system, since in (143) we could have $s_1, s_2, \cdots, s_N$ equal to each other. For distinguishable particles system, there is no problem since if we have two particle staying at the same state, we can distinguish them, thus (Particle-A @ state-1, Particle-B @ state-2) and (Particle-A @ state-2, Particle-B @ state-1) are different. However for indistinguishable particles, the above two states are actually the same since we cannot distinguish between particle-A and particle-B! Thus for the N-particle canonical partition function given by (143), we have overcounted the states for indistinguishable particles system. Then what is the overcounting? To make it clear, it's better to write (143) in another way:

$$Z_N = \sum_s e^{-N\beta\epsilon_s} + \sum_{s_1}\sum_{s_2}\cdots\sum_{s_N} e^{-\beta(\epsilon_{s_1}+\epsilon_{s_2}+\cdots+\epsilon_{s_N})} \tag{144}$$

where the first term corresponds to the case when all the N particles are at the same state, and the second term refers to all states from s_1 to s_N are different. Actually we should have other terms corresponding to the case when some particles are at the same state and some are at other states. Indeed we should have, but since the probability of several particles staying at the same state is quite small, we can actually ignore the contribution from them. Thus it is not necessary to worry about those complex terms, including the first term in (144)! Then we are left with the second term in (144), where all particles are in different states of the system. However, since particles are indistinguishable, we have overcounting the states by $N!$. To understand this, just imagine the example of three-particles system, where we have particle A, B and C, and they are indistinguishable from each other. Thus the following distribution of partilces are actually the same: (A @ state-1, B @ state-2, C @ state-3), (A @ state-1, B @ state-3, C @ state-2), (A @ state-2, B @ state-1, C @ state-3), (A @ state-2, B @ state-3, C @ state-1), (A @ state-3, B @ state-1, C @

state-2) and (A @ state-3, B @ state-2, C @ state-1). So we know that the overcounting factor is just the permutation of the number of particles in the system — for N-particles system, it is $N!$. Therefore the N indistinguishable particles canonical partition function should be given by:

$$Z_N = \frac{1}{N!}\sum_{s_1}\sum_{s_2}\cdots\sum_{s_N} e^{-\beta(\epsilon_{s_1}+\epsilon_{s_2}+\cdots+\epsilon_{s_N})} = \frac{1}{N!}Z_1^N \tag{145}$$

As we already pointed out, the contribution from the term for which there are some particles at the same state is small, so in (145), it is not necessary to restrict $s_1, s_2, \cdots, s_N$ are different from each other any more.