# Assignment: Statistical Mechanics

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# Exercise 1. Give the full details for the derivation of the standard deviation of the number of particles in the grand canonical ensemble

The partition function is defined as:

$$\Xi = \sum_{N=0}^{\infty} \sum_{\nu} e^{-\beta(E_{N,\nu}-\mu N)} \tag{1}$$

And the probability:

$$P_{N,\nu} = \frac{e^{-\beta(E_{N,\nu}-\mu N)}}{\Xi} \tag{2}$$

The mean number of particles is given by:

$$\langle N \rangle = \sum_{N=0}^{\infty} N \, P(N) \tag{3}$$

From the definition of $P(N)$:

$$P(N) = \frac{e^{\beta\mu N} Z_N}{\Xi}, \quad \text{where } Z_N = \sum_{\nu} e^{-\beta E_{N,\nu}} \text{ (sum of all microstates with } N \text{ particles).} \tag{4}$$

Using this, we write:

$$\langle N \rangle = \frac{1}{\Xi} \sum_{N=0}^{\infty} N \, e^{\beta\mu N} Z_N \tag{5}$$

On the other hand:

$$\left(\frac{\partial \Xi}{\partial \mu}\right)_{T,V} = \sum_{N=0}^{\infty} \sum_{\nu} e^{-\beta E_{N,\nu}} \cdot \beta N \cdot e^{\beta\mu N} = \beta \sum_{N=0}^{\infty} \sum_{\nu} N \cdot e^{-\beta(E_{N,\nu}-\mu N)} \tag{6}$$

For a fixed number of particles $N$:

$$\left(\frac{\partial \Xi}{\partial \mu}\right)_{T,V} = \beta \sum_{N=0}^{\infty} N \cdot e^{\beta\mu N} \cdot Z_N \tag{7}$$

Comparing equations 5 and 7 we can deduce:

$$\boxed{\langle N \rangle = \sum_{N=0}^{\infty} N \, P(N) = \frac{1}{\Xi} \sum_{N=0}^{\infty} N \, e^{\beta\mu N} Z_N = \frac{1}{\beta\Xi} \left(\frac{\partial \Xi}{\partial \mu}\right)_{T,V} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{T,V}} \tag{8}$$

To calculate the variance, we take the second derivative:

$$\frac{1}{\beta}\frac{\partial^2 \ln \Xi}{\partial \mu^2} = \frac{\partial}{\partial \mu}\left(\frac{1}{\beta}\frac{\partial \ln \Xi}{\partial \mu}\right).$$

(9)

Expanding this derivative:

$$\frac{1}{\beta}\frac{\partial^2 \ln \Xi}{\partial \mu^2} = \frac{1}{\beta}\left[-\left(\frac{1}{\Xi}\frac{\partial \Xi}{\partial \mu}\right)^2 + \frac{1}{\Xi}\frac{\partial^2 \Xi}{\partial \mu^2}\right] = \left(\frac{\partial^2 \ln \Xi}{\partial \mu^2} - \left(\frac{\partial \ln \Xi}{\partial \mu}\right)^2\right)\cdot\frac{1}{\beta}.$$

(10)

Using equation 8, the first term:

$$\frac{\partial^2 \ln \Xi}{\partial \mu^2}\cdot\frac{1}{\beta} = \langle N^2\rangle$$

(11)

The second term:

$$\left(\frac{\partial \ln \Xi}{\partial \mu}\right)^2\cdot\frac{1}{\beta} = \langle N\rangle^2$$

(12)

We can write the variance as:

$$\boxed{\sigma^2(N) = \langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta}\left(\frac{\partial^2 \ln \Xi}{\partial \mu^2}\right)_{T,V} = \frac{1}{\beta}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V}}$$

(13)

Using Equation 1.35 of Chapter 1

$$\left(\frac{\partial \mu}{\partial \langle N\rangle}\right)_{T,V} = -\frac{V^2}{\langle N\rangle^2}\left(\frac{\partial P}{\partial V}\right)_{T,N}$$

(14)

$$\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = -\frac{\langle N\rangle^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

(15)

Substituting in equation 13:

$$\sigma^2(N) = -\frac{k_B T\langle N\rangle^2}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,N}$$

(16)

Using Equation 1.36 of Chapter 1

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N} \quad\Rightarrow\quad \left(\frac{\partial V}{\partial P}\right)_{T,N} = -Vk_T$$

(17)

Substituting in equation 16:

$$\sigma^2(N) = \frac{k_B T\langle N\rangle^2 k_T}{V}$$

(18)

$$\boxed{\frac{\sigma(N)}{\langle N \rangle} = \left( \frac{k_B T k_T}{V} \right)^{1/2}} \tag{19}$$

For an Ideal Gas:

$$PV = \langle N \rangle k_B T \quad \Rightarrow \quad V = \frac{\langle N \rangle k_B T}{P} \tag{20}$$

Deriving:

$$\left( \frac{\partial V}{\partial P} \right)_{T,N} = -\frac{\langle N \rangle k_B T}{P^2} \tag{21}$$

Using equation 17:

$$k_T = \frac{1}{V} \cdot \frac{\langle N \rangle k_B T}{P^2} \tag{22}$$

Substituting the volume in equation 20:

$$k_T = \frac{1}{\langle N \rangle k_B T} \cdot \frac{\langle N \rangle k_B T}{P} = \frac{1}{P} \tag{23}$$

Using equations 20 and 23:

$$\langle N \rangle = \frac{PV}{k_B T} = \frac{V}{k_B T k_T} \tag{24}$$

Finally:

$$\boxed{\frac{\sigma^2(N)}{\langle N \rangle} = \left( \frac{1}{\langle N \rangle} \right)^{1/2}} \tag{25}$$

# Exercise 2. A surface presenting $N_0$ traps that can absorb one atom each. The energy of one absorbed atom is $-\varepsilon_0$ $(\varepsilon_0 > 0)$.

## a) Obtain the grand partition function, $\Xi$, the average number of particles $N_a$, and the corresponding energy.

The energy only depends on the number of atoms:

$$E = -N\varepsilon_0 \tag{26}$$

For a fixed $N$, there is exactly one energy. Also, for a fixed number of atoms $N$, there are $\binom{N_0}{N}$ ways of distributing the atoms along the $N_0$ traps. Each of these distributions corresponds to one microstate with energy $-N\varepsilon_0$.

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The macrocanonical partition function is:

$$\Xi = \sum_{N=0}^{\infty} \sum_{\nu} e^{-\beta(E_{N,\nu} - \mu N)} \tag{27}$$

Taking into account the sum of the energies of all microstates:

$$\Xi = \sum_{N=0}^{N_0} \binom{N_0}{N} e^{-\beta(-N\varepsilon_0 - \mu N)} \tag{28}$$

$$= \sum_{N=0}^{N_0} \binom{N_0}{N} \left(e^{\beta(\varepsilon_0 + \mu)}\right)^N \tag{29}$$

Here we can use the binomial expansion:

$$(a+b)^n = \sum_{k=0}^{n} \binom{n}{k} a^k b^{n-k} \tag{30}$$

Applying this to the partition function in equation 29:

$$\boxed{\Xi = \left(1 + e^{\beta(\varepsilon_0 + \mu)}\right)^{N_0}} \tag{31}$$

As it was deduced in equation 8 the average number of particles is:

$$N_a = \langle N \rangle = k_B T \left(\frac{\partial \ln \Xi}{\partial \mu}\right)_{T,V} \tag{32}$$

Substituting:

$$\ln \Xi = N_0 \ln \left(e^{\beta(\varepsilon_0 + \mu)} + 1\right) \tag{33}$$

Deriving:

$$\frac{\partial \ln \Xi}{\partial \mu} = N_0 \frac{\partial}{\partial \mu} \ln \left(e^{\beta(\varepsilon_0 + \mu)} + 1\right) = N_0 \frac{\beta e^{\beta(\varepsilon_0 + \mu)}}{1 + e^{\beta(\varepsilon_0 + \mu)}} \tag{34}$$

Substituting in equation 32:

$$\boxed{N_a = \langle N \rangle = N_0 \frac{e^{\beta(\varepsilon_0 + \mu)}}{1 + e^{\beta(\varepsilon_0 + \mu)}}} \tag{35}$$

The average number of particles is the number of traps times the probability of each trap being occupied.

- At high temperatures $(T \to \infty, \beta \to 0)$:

$$\langle N \rangle \to N_0 \cdot \frac{1}{2} \tag{36}$$

- At low temperatures $(T \to 0, \beta \to \infty)$:

$$\langle N \rangle \to N_0 \tag{37}$$

We substitute in equation 26 to obtain the energy corresponding to the average number of particles:

$$\boxed{E = -N_a \epsilon_0 = -\epsilon_0 N_0 \frac{e^{\beta(\varepsilon_0 + \mu)}}{1 + e^{\beta(\varepsilon_0 + \mu)}}} \tag{38}$$

## b) We assume now that the surface is in fact the wall of the recipient of volume V containing the gas and that it is formed of the same atoms as the gas.

## i) Express the chemical potential as a function of the pressure P, and the temperature T

In an ideal gas the canonical partition function is:

$$Z_N = \frac{q^N}{N!} \tag{39}$$

Where

$$q = \frac{V}{\Lambda^3} \quad with \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \tag{40}$$

In order to get the grand canonical partition function of the system:

$$\Xi = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_N \tag{41}$$

$$\Xi = \sum_{N=0}^{\infty} \frac{\left(e^{\beta \mu} \cdot q\right)^N}{N!} \tag{42}$$

We can use the Taylor expansion of $e^x$:

$$e^x = \sum_{N=0}^{\infty} \frac{x^N}{N!} \quad \Rightarrow \quad \Xi = e^{\left(e^{\beta \mu} \cdot q\right)} \tag{43}$$

So the grand canonical partition function of this system is:

$$\Xi = e^{\left(e^{\beta \mu} \cdot \frac{V}{\Lambda^3}\right)} \tag{44}$$

To obtain the chemical potential as a function of P and T we can use the relation:

$$PV = k_B \ln \Xi \tag{45}$$

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Thus:

$$PV = k_B T \cdot e^{\beta\mu} \frac{V}{\Lambda^3} \tag{46}$$

Simplifying:

$$\frac{P\Lambda^3}{k_B T} = e^{\beta\mu} \tag{47}$$

Finally the expression for the chemical potential is:

$$\boxed{\mu = \frac{1}{\beta} \ln \frac{P\Lambda^3}{k_B T}} \tag{48}$$

## ii) Derive the Langmuir's adsorption isotherm

$\theta$ is the fraction of adsorption sites occupied by adsorbate. We can use equation 35:

$$\theta = \frac{N}{N_0} = \frac{e^{\beta(\varepsilon_0 + \mu)}}{1 + e^{\beta(\varepsilon_0 + \mu)}} \tag{49}$$

Now $\mu$ is substituted using the expression for the chemical potential of the gas phase in equation 48:

$$\Theta = \frac{e^{\beta\epsilon_0} \cdot e^{\ln\left(\frac{P\Lambda^3}{k_B T}\right)}}{1 + e^{\beta\epsilon_0} \cdot e^{\ln\left(\frac{P\Lambda^3}{k_B T}\right)}} \tag{50}$$

Simplifying:

$$\Theta = \frac{e^{\beta\epsilon_0} \frac{P\Lambda^3}{k_B T}}{1 + e^{\beta\epsilon_0} \frac{P\Lambda^3}{k_B T}} \tag{51}$$
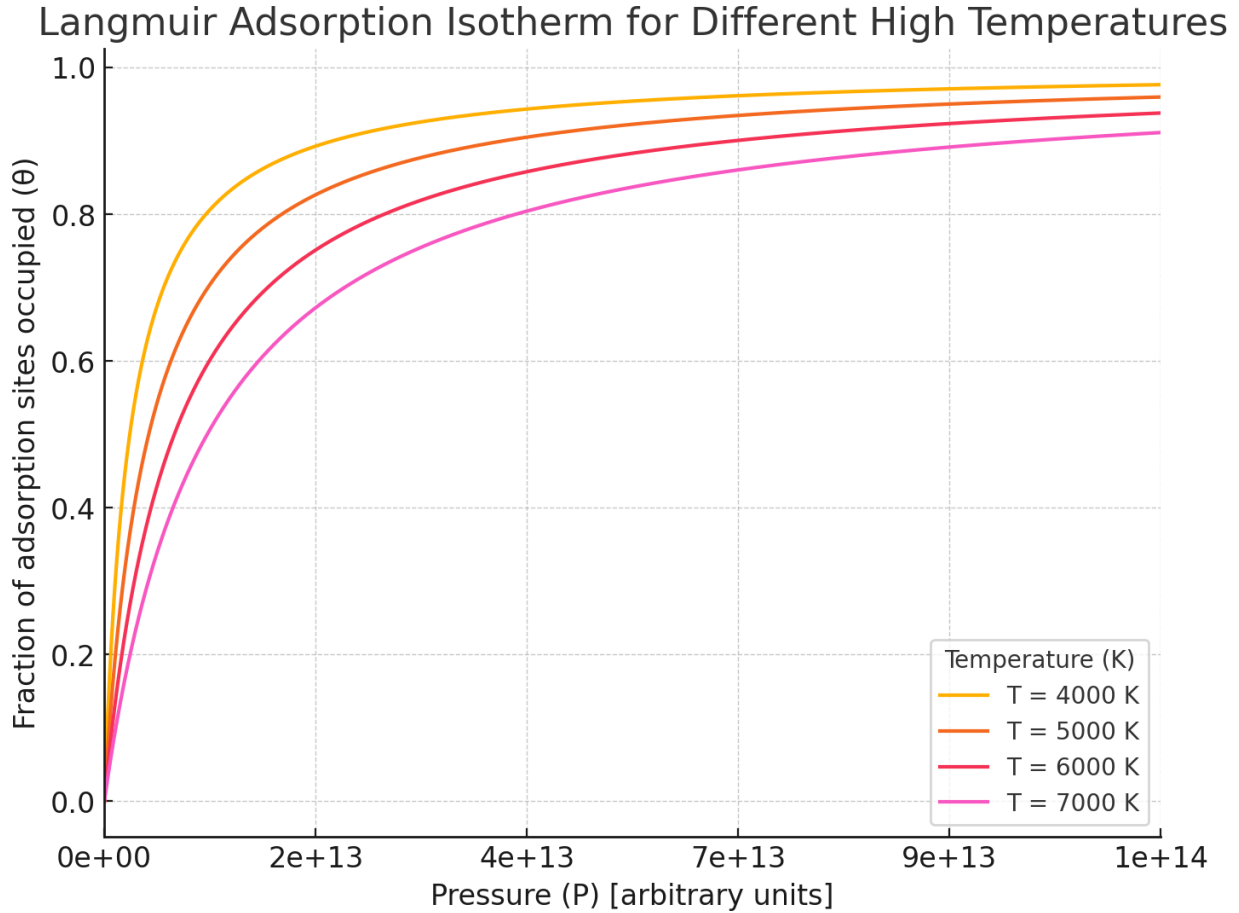
Finally we get the Langmuir's adsorption isotherm:

$$\boxed{\Theta = \frac{b(T)P}{1 + b(T)P}} \tag{52}$$

Where $b(T)$ is a function of temperature:

$$b(T) = \beta\Lambda^3 e^{\beta\epsilon_0} \quad \text{with} \quad \beta = \frac{1}{k_B T} \quad \text{and} \quad \Lambda = \frac{h}{(2\pi m k_B T)^{1/2}} \tag{53}$$

## iii) Plot $\theta$ versus P for different constant temperatures and comment the results



In this graph we can see the relation between the fraction of adsorption sites occupied by adsorbate changes with the pressure at different temperatures. At low pressures, adsorption increases rapidly as pressure rises. At higher pressures, adsorption slows down and approaches a maximum value $\theta=1$. We can also see the effect of the temperature, as temperature increases, adsorption becomes less efficient. This means fewer sites are occupied at the same pressure, this makes sense with the result of mean number of particles expressed in equation 36.

## Exercise 3. Based on classical statistical mechanics, the canonical partition function for an ideal monoatomic gas is:

$$Q = \frac{V^N}{N!} \left(2\pi m k_B T\right)^{3N/2} \frac{1}{h^{3N}} \tag{54}$$

## a) Obtain the expression for the Helmholtz free energy

The Helmholtz free energy is:

$$A = -k_B T \ln Q \tag{55}$$

$$Q = \frac{1}{N!} \cdot \left( \frac{V \cdot (2\pi m k_B T)^{3/2}}{h^3} \right)^N = \frac{1}{N!} \left( \frac{V}{\Lambda^3} \right)^N \quad with \ \Lambda = \frac{h}{(2\pi m k_B T)^{\frac{1}{2}}}$$

Taking the logarithm:

$$
\begin{aligned}
\ln Q &= \ln \left( \frac{1}{N!} \cdot \left( \frac{V}{\Lambda^3} \right)^N \right) \\
&= \ln \left( \frac{1}{N!} \right) + \ln \left( \left( \frac{V}{\Lambda^3} \right)^N \right) \\
&= -\ln N! + N \ln \left( \frac{V}{\Lambda^3} \right).
\end{aligned}
\tag{56}
$$

We can use Stirling's approximation for large $N$:

$$\ln N! \approx N \ln N - N \tag{57}$$

We get:

$$\ln Q = -N \ln N + N + N \ln \left( \frac{V}{\Lambda^3} \right) = N \left[ \ln \left( \frac{V}{N\Lambda^3} \right) + 1 \right]. \tag{58}$$

Therefore, the Helmholtz free energy is:

$$\boxed{A = -k_B T \ln Q = -k_B T N \left[ \ln \left( \frac{V}{N\Lambda^3} \right) + 1 \right]} \tag{59}$$

## b) Obtain the chemical potential

The chemical potential is given by:

$$\mu = \left( \frac{\partial A}{\partial N} \right)_{T,V} \tag{60}$$

Using the expression for $A$ in equation 59:

$$\mu = \left( \frac{\partial A}{\partial N} \right)_{T,V} = -k_B T \cdot \left[ \ln \left( \frac{V}{\Lambda^3 N} \right) + 1 \right] - k_B T N \cdot \frac{\partial}{\partial N} \left[ \ln \left( \frac{V}{\Lambda^3 N} \right) + 1 \right] \tag{61}$$

$$\mu = -k_B T \cdot \left[ \ln \left( \frac{V}{\Lambda^3 N} \right) + 1 \right] + k_B T \tag{62}$$

Finally:

$$\boxed{\mu = -k_B T \cdot \left[ \ln \left( \frac{V}{\Lambda^3 N} \right) \right]} \tag{63}$$

## c) Obtain the pressure

The pressure is given by:

$$P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{T,V} \tag{64}$$

The logarithm of the partition function $Q$ from equation 58 is:

$$\ln Q = N \left[ \ln \left( \frac{V}{\Lambda^3 N} \right) + 1 \right], \tag{65}$$

We derive $\ln Q$ with respect to $V$:

$$\begin{aligned} \frac{\partial \ln Q}{\partial V} &= \frac{\partial}{\partial V} \left[ N \ln \left( \frac{V}{\Lambda^3 N} \right) + N \right] \\ &= N \frac{\partial}{\partial V} \ln V \\ &= \frac{N}{V}. \end{aligned} \tag{66}$$

The pressure $P$ is related to the derivative of $\ln Q$ as:

$$\boxed{P = k_B T \frac{\partial \ln Q}{\partial V} = k_B T \frac{N}{V}.} \tag{67}$$

From equation 67 we can get the ideal gas law:

$$\boxed{PV = \frac{N_A}{N_A} k_B T N = nRT,} \tag{68}$$

where $N_A$ is Avogadro's number, $n = \frac{N}{N_A}$ is the number of moles, and $R = N_A k_B$ is the universal gas constant.

## d) Obtain the entropy

The entropy is given by:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}.$$
(69)

The Helmholtz free energy from equation 59 is:

$$A = -Nk_BT\ln\left(\frac{V}{N\Lambda^3}\right) - Nk_BT,$$
(70)

The derivative of the Helmholtz free energy $A$ with respect to $T$ is given by:

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} = -k_BN\cdot\left[\ln\left(\frac{V}{\Lambda^3 N}\right)+1\right] - k_BTN\cdot\frac{\partial}{\partial T}\left(\ln\left(\frac{V}{\Lambda^3 N}\right)+1\right)_{V,N}.$$
(71)

Simplifying the second term:

$$\frac{\partial}{\partial T}\left(\ln\left(\frac{V}{\Lambda^3 N}\right)+1\right)_{V,N} = \frac{\partial}{\partial T}\left[\ln\frac{V}{N} - 3\ln\Lambda + 1\right]_{V,N}$$

$$= -3\cdot\left(\frac{\partial\ln\Lambda}{\partial T}\right)_{V,N}$$
(72)

$$= -\frac{3}{\Lambda}\cdot\left(\frac{\partial\Lambda}{\partial T}\right)_{V,N}$$

$$= -\frac{3}{\Lambda}\cdot\left(\frac{\partial}{\partial T}\left(\frac{h}{\sqrt{2\pi mk_BT}}\right)\right)_{V,N}$$
(73)

$$= \frac{3}{2\Lambda}\cdot\left(\frac{h}{(2\pi mk_BT)^{1/2}\cdot T}\right) = \frac{3\Lambda}{2\Lambda T} = \frac{3}{2T}$$

Substituting back into the original equation 69:

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} = -k_BN\cdot\left[\ln\left(\frac{V}{\Lambda^3 N}\right)+1\right] - k_BTN\cdot\frac{3}{2T}.$$
(74)

Simplifying:

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} = -k_BN\left[\ln\left(\frac{V}{\Lambda^3 N}\right)+\frac{5}{2}\right]$$
(75)

Finally, the entropy is:

$$\boxed{S = k_BN\left[\ln\left(\frac{V}{\Lambda^3 N}\right)+\frac{5}{2}\right]}$$
(76)

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### e) Internal energy and heat capacity at constant volume

The internal energy is defined as:

$$U = -\frac{\partial \ln Q}{\partial \beta}, \quad \text{where } \beta = \frac{1}{k_B T}. \tag{77}$$

The logarithm of the partition function from equation 58 is:

$$\ln Q = -N \ln N + N + N \ln V - N \ln \Lambda^3 \tag{78}$$

We derive with respect to $\beta$:

$$\frac{\partial \ln Q}{\partial \beta} = \frac{\partial}{\partial \beta} \left( -N \ln N + N + N \ln V - N \ln \Lambda^3 \right) \tag{79}$$

$$= \frac{\partial}{\partial \beta} \left( -N \ln \Lambda^3 \right) \tag{80}$$

$$= \frac{\partial}{\partial \beta} \left( -N \ln \left( \frac{h^3}{(2\pi m k_B T)^{3/2}} \right) \right) \tag{81}$$

$$= -N \cdot \frac{\partial}{\partial \beta} \left( -\ln (2\pi m k_B T)^{3/2} \right) \tag{82}$$

$$= -N \cdot \frac{\partial}{\partial \beta} \left( -\frac{3}{2} \ln (k_B T) \right) \tag{83}$$

$$= \frac{3}{2} N \frac{\partial}{\partial \beta} \left( \ln \frac{1}{\beta} \right) \tag{84}$$

$$= -\frac{3}{2\beta} N. \tag{85}$$

Finally the internal energy is:

$$\boxed{U = \frac{3N k_B T}{2}} \tag{86}$$

The heat capacity at constant volume $C_V$ is given by:

$$\boxed{C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T} \left( \frac{3}{2} N k_B T \right) = \frac{3}{2} N k_B.} \tag{87}$$

The equipartition theorem states that for each particle, each degree of freedom contributes as $\frac{1}{2} k_B T$ to the total energy so:

$$U = Degrees\,of\,Freedom \cdot \frac{1}{2} k_B T \tag{87}$$

A monoatomic gas has three degrees of freedom, contributing $\frac{1}{2}k_BT$ per degree of freedom to the total energy.

$$U = 3 \cdot \frac{1}{2}k_BT \tag{88}$$

This result matches the previously derived result for $U$ and the heat capacity $C_V$.

# Exercise 4

### a) Number of quantum states with energy less than or equal to $\epsilon$ for a particle in a three-dimensional square box of edge length $a$

The energy of a particle in a three-dimensional box is given by:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \tag{89}$$

Any state with energy lower or equal to $\epsilon$ fulfills:

$$E_{n_x,n_y,n_z} \leq \epsilon \tag{90}$$

$$(n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8ma^2} \leq \epsilon \tag{91}$$

$$n_x^2 + n_y^2 + n_z^2 \leq \frac{8ma^2\epsilon}{h^2} \tag{92}$$

Every one of these states will be inside of an imaginary sphere with radius $R$ that corresponds to the maximum energy:

$$n_x^2 + n_y^2 + n_z^2 \leq R^2, \quad R^2 = \frac{8ma^2\epsilon}{h^2} \tag{93}$$

So in order to calculate the number of states we use the volume of this sphere:

$$V_{\text{total}} = \frac{4}{3}\pi R^3 \tag{94}$$

Since the quantic numbers are positive, they are inside an octant:

$$V_{\text{octant}} = \frac{1}{8} \cdot \frac{4}{3}\pi R^3 = \frac{\pi}{6}R^3 \tag{95}$$

The number of states will always be smaller than the volume of the octant. As $R$ is bigger, the number of states will be closer to the volume of the octant:

$$N(\epsilon) \approx \frac{\pi}{6}R^3 \quad , \quad \text{When R is very big} \tag{96}$$

Substituting R in equation number 93 we get:

$$\boxed{N(\epsilon) \leq \frac{\pi}{6} \cdot \left(\frac{8ma^2\epsilon}{h^2}\right)^{3/2}} \tag{97}$$

## b) Discuss the influence of the mass of the particles, the temperature and the (number) density

The influence of the mass, temperature and numeric density is important because they are the conditions that determine whether Boltzmann statistics are valid or not.

Boltzmann statistics can only be applied when the number of accessible states $N(\epsilon)$ is much bigger than the number of particles $N$:

$$\frac{N(\epsilon)}{N} \gg 1 \tag{98}$$

For particles with large mass, there will be much more accessible states since $N(\epsilon) \propto m^{3/2}$, which means that Boltzmann statistics can be applied.

Temperature also affects the ratio $N(\epsilon)/N$. The internal energy is proportional to $k_B T$

$$\langle \epsilon \rangle = \frac{1}{2} k_B T \quad \text{, in each degree of freedom} \tag{99}$$

And $N(\epsilon) \propto \epsilon^{3/2}$ .Thus, this means that for high temperatures, the number of accessible states is much bigger than the number of particles, and Boltzmann statistics will be valid.

Finally, the numeric density is important because with lower densities there will be much more quantum states accessible, and Boltzmann statistics will be valid.

Small particles at low temperature and high densities favor quantum effects, and Boltzmann statistics will not be valid.

## c) Derive the number of states with energy in between $\epsilon$ and $\epsilon + d\epsilon$

The number of states is:

$$N(\epsilon) = \frac{\pi}{6} \left( \frac{8ma^2\epsilon}{h^2} \right)^{3/2} \tag{100}$$

We derive over $d\epsilon$:

$$\frac{\partial N(\epsilon)}{\partial \epsilon} = \frac{\pi}{6} \left( \frac{8ma^2}{h^2} \right)^{3/2} \cdot \frac{3}{2} \cdot \epsilon^{1/2} \tag{101}$$

So the number of states between $\epsilon$ and $\epsilon + d\epsilon$ is:

$$\boxed{dN(\epsilon) = \frac{\pi}{4} \left( \frac{8ma^2}{h^2} \right)^{3/2} \epsilon^{1/2} \, d\epsilon} \tag{102}$$

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The number of states with energy between $\epsilon$ and $\epsilon + d\epsilon$ for an ideal gas of fermions is:

$$g(\epsilon)\,d(\epsilon) = 4\pi \left(\frac{2m}{h^2}\right)^{3/2} V\,\epsilon^{1/2}\,d\epsilon \tag{103}$$

To compare it with the number of states of a particle in a box we calculate the relation:

$$\frac{dN(\epsilon)}{g(\epsilon)\,d(\epsilon)} = \frac{\frac{\pi}{4}\left(\frac{8ma^2}{h^2}\right)^{3/2}\epsilon^{1/2}\,d\epsilon}{4\pi\left(\frac{2m}{h^2}\right)^{3/2}V\,\epsilon^{1/2}\,d\epsilon} \tag{104}$$

$$= \frac{\frac{1}{4}\cdot 8^{\frac{3}{2}}\cdot a^3}{4\cdot 2^{\frac{3}{2}}\cdot V} \tag{105}$$

$$= \frac{1}{2}\cdot \frac{a^3}{V} \tag{106}$$

Since the number of states of the numerator refers to a particle in a box of length a, then $a^3 = V$, so:

$$\boxed{\frac{dN(\epsilon)}{g(\epsilon)\,d(\epsilon)} = \frac{1}{2}} \tag{107}$$

The number of states of the ideal gas of fermions is the double of the number of states of a particle in a box.

This is because fermions can have two different quantic states for each energy state since they have two possible spins.

## d) Derive the number of states with momentum in between $p$ and $p + dp$. Starting with $dN(\epsilon) = dN(p)$

Starting with:

$$dN(\epsilon) = dN(p) \tag{108}$$

The relation between energy and momentum is:

$$\epsilon = \frac{p^2}{2m}, \quad \frac{d\epsilon}{dp} = \frac{p}{m} \tag{109}$$

Since:

$$dN(\epsilon) = \frac{\pi}{4}\left(\frac{8ma^2}{h^2}\right)^{3/2}\epsilon^{1/2}\,d\epsilon \tag{110}$$

Therefore:

$$dN(p) = \frac{\pi}{4}\left(\frac{8ma^2}{h^2}\right)^{3/2}\frac{p}{\sqrt{2m}}\cdot\frac{p}{m}\,dp \tag{111}$$

Simplifying:

$$dN(p) = \frac{\pi}{4\sqrt{2}} \left(\frac{8a^2}{h^2}\right)^{3/2} p^2 \, dp \tag{112}$$

Finally:

$$\boxed{dN(p) = 4\pi \left(\frac{a}{h}\right)^3 p^2 \, dp} \tag{113}$$

## e) Derive the number of states with frequency between $\nu$ and $\nu + d\nu$

The relation between frequency and momentum is:

$$p = \frac{h\nu}{c}, \quad \frac{dp}{d\nu} = \frac{h}{c} \tag{114}$$

Since:

$$dN(p) = 4\pi \left(\frac{a}{h}\right)^3 p^2 \, dp \tag{115}$$

and:

$$dN(p) = dN(\nu) \tag{116}$$

Then:

$$dN(\nu) = 4\pi \left(\frac{a}{h}\right)^3 \left(\frac{h^2\nu^2}{c^2}\right) \frac{h}{c} \, d\nu \tag{117}$$

Simplifying:

$$\boxed{dN(\nu) = 4\pi \left(\frac{a}{c}\right)^3 \nu^2 \, d\nu} \tag{118}$$

In the case of photons, the number of states with frequency between $\nu$ and $\nu + d\nu$ is:

$$g(\nu) = 8\pi V \frac{\nu^2}{c^3} \tag{119}$$

When we compare equation 118 with equation 119 we can see that the number of states with frequency between $\nu$ and $\nu + d\nu$. Having in mind that for a particle in a box $V = a^3$

This difference can be explained by the fact that photons have two polarization configurations, which means that for each frequency, a photon can be in two different states.

# Exercise 5. Consider the Debye model for the crystalline solid

**a) Using Eq. (4.8) of the slide presentation and the Debye frequency distribution function. Obtain the expression of the internal energy of the crystal**

Using Eq. 4.8 of the presentation:

$$E = E_0 + \int_0^\infty \frac{g(\nu)h\nu}{e^{\beta h\nu} - 1} d\nu \tag{120}$$

With:

$$g(\nu) = \frac{9N\nu^2}{\nu_D^3} \tag{121}$$

Therefore:

$$E = \int_0^{\nu_D} \frac{9N\nu^2 h\nu}{\nu_D^3(e^{\beta h\nu} - 1)} d\nu \tag{122}$$

Integrating:

$$E = \frac{9Nh}{\nu_D^3} \int_0^{\nu_D} \frac{\nu^3}{e^{\beta h\nu} - 1} d\nu \tag{123}$$

Applying a variable change:

$$x = h\nu\beta; \quad \nu = \frac{x}{h\beta} \quad \rightarrow \quad d\nu = \frac{1}{h\beta} dx \tag{124}$$

The new integration limits are:

$$\nu = 0 \rightarrow x = h \cdot 0 \cdot \beta = 0 \tag{125}$$
$$\nu = \nu_D \rightarrow x = h\nu_D\beta = x_D \tag{126}$$

Then:

$$E = \frac{9Nh}{\left(\frac{x_D}{h\beta}\right)^3} \int_0^{x_D} \frac{\left(\frac{x}{h\beta}\right)^3}{e^x - 1} \cdot \frac{1}{h\beta} dx \tag{127}$$

$$= \frac{9Nh^4\beta^3}{(h\beta)^4 x_D^3} \cdot \int_0^{x_D} \frac{x^3}{e^x - 1} dx \tag{128}$$

Simplifying:

$$E = \frac{9N}{\beta x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx \tag{129}$$

Finally:

$$\boxed{E = \frac{3N}{\beta} \cdot D(x_D) \quad \text{with} \quad D(x_D) = \frac{3}{x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx} \tag{130}$$

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**5b) Using the Debye model, the expression of the entropy is:**

$$S = Nk_B \left[ 4D(x_D) - 3\ln\left(1 - e^{-x_D}\right) \right] \tag{131}$$

To evaluate the entropy when the temperature becomes zero:

$$x_D = \frac{\Theta_D}{T}, \quad \text{so when } T \to 0,\, x_D \to \infty$$

$$\lim_{x_D \to \infty} S = \lim_{x_D \to \infty} Nk_B \left[ 4D(x_D) - 3\ln\left(1 - e^{-x_D}\right) \right] \tag{132}$$

The first term:

$$\lim_{x_D \to \infty} \left( \cdot 4 \cdot \frac{3}{x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx \right) = \frac{3}{\infty} \cdot \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{3}{\infty} \cdot \frac{\pi^4}{5} = 0 \tag{133}$$

So the first term tends to zero.

The second term:

$$\lim_{x_D \to \infty} \left[ -3Nk_B \ln\left(1 - e^{-x_D}\right) \right] = \lim_{x_D \to \infty} \left[ \ln\left(1 - e^{-x_D}\right) \right] = \ln(1) = 0 \tag{134}$$

Final result:

$$\lim_{x_D \to \infty} S = \lim_{x_D \to \infty} Nk_B \left(0 - 0\right) = 0 \tag{135}$$

When $T \to 0$, the entropy $S \to 0$.

# 5c) Calculate the temperature at which the internal energy of copper $(\theta_D = 308K)$ is $\frac{2}{3}$ of its classical value.

Classical and Debye energies:

$$E_{\text{classical}} = 3Nk_BT \tag{136}$$

$$E_{\text{Debye}} = 3Nk_BT \cdot D(x_D) \tag{137}$$

Since the energy has to be $\frac{2}{3}$ of the classical:

$$D(x_D) = \frac{2}{3} \approx 0.667 \tag{138}$$

Using the Debye table:

$$D(1) \approx 0.6744 \tag{139}$$

So $x_D \approx 1$.

$$x_D = \frac{\Theta_D}{T}, \quad T \approx \frac{\Theta_D}{x_D} \approx \frac{308}{1} = 308\,\text{K} \tag{140}$$