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1. Learning Outcomes

After studying this module, you shall be able to

- Apply the approach of canonical ensemble via partition function to two very important prototype systems in physics via partition function
    - A collection of harmonic oscillators (classical and quantum mechanical treatment)
    - Para-magnetism (classical and quantum mechanical treatment).
- Compare the classical and quantum mechanical results obtained in the above two examples and see under what conditions quantum mechanical results approach classical results.
- To appreciate equipartition theorem and virial theorems as classical canonical ensemble averages of the quantity $\boldsymbol{X_a}\frac{\partial \boldsymbol{H}}{\partial \boldsymbol{X_b}}$, where $\boldsymbol{X_a}$ and $\boldsymbol{X_b}$ are any two of the phase space co-ordinates of the system.
- To apply equipartition theorem to derive some well-known results for systems such as monoatomic gas, a diatomic gas, a harmonic oscillator and a crystalline solid.
- Derive virial theorem.
- Understand the importance of virial in computation of equation of state of a system and paving way for calculating pressure of the system.
- Calculate density of states over energy for a three dimensional system of free particles in non-relativistic, relativistic and ultra-relativistic regime.

2. Introduction

In this module we carry forward the applications of canonical ensemble two most important problems of the physics: a collection of harmonic oscillators and classical model of para-magnetism treated as a system of N magnetic dipoles. Also we shall encounter two beautiful theorems called virial theorem of Clausius and equipartition theorem of Boltzmann. These theorems have many applications to arrive at some useful results in thermodynamics and statistical mechanics.

3. Canonical Ensemble (More Applications)

Now we will look at some more interesting applicationsof canonical ensemble and simplicity with results can be obtained using partition function approach.

3.1 A System of Harmonic Oscillators

Let us now examine a collection of N independent identical Linear harmonic oscillators using partition function approach as an application of canonical ensemble which forms a precursor to the study the statistical mechanics of a collection of photons in black body radiation and a collection of phonons in theory of lattice vibrations in solids. We treat the oscillators as first as classical entities and later as quantum mechanical entities to get the thermodynamics of the system and compare the results for any change in going from classical system of harmonic oscillators to quantum mechanical system of harmonic oscillators.

The Hamiltonian for a this set of identical linear harmonic oscillators, each having mass m and frequency $\boldsymbol{\omega}$ is given by

$$\boldsymbol{H} = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 q_i^2\right) \tag{1}$$

(a) Classical Approach

Now we are ready to write a one particle partition function for the recalling the definition in the Module 13.

$$Z_1 = \frac{1}{h}\int e^{-\beta H_i(q_i,p_i)} d^3q_i d^3\mathrm{p_i} \tag{2}$$

$$= \frac{1}{h}\int e^{-\frac{\beta p_i^2}{2m}} d^3p_i \int e^{-\frac{1}{2}\beta m\omega^2 q_i^2}\, d^3\mathrm{q_i}$$

$$Z_1 = \frac{1}{h}\left(\frac{2m\pi}{\beta}\right)^{\frac{1}{2}}\left(\frac{2\pi}{\beta m\omega^2}\right)^{\frac{1}{2}} = \frac{1}{\beta\hbar\omega} \tag{3}$$

Here $\boldsymbol{\beta} = \frac{1}{k_BT}$. The partition function for the collection of independent N linear harmonic oscillators can be written as

$$Z = Z_1^N = (\beta\hbar\omega)^{-N} \tag{4}$$

Now all thermodynamic properties can be derived

Helmholtz free energy (F)

$$F = -k_BT\ln Z = Nk_BT\ln\beta\hbar\omega = Nk_BT\ln\frac{\hbar\omega}{k_BT} \tag{5}$$

Entropy (S)

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = Nk_B\left[1 - \ln\frac{\hbar\omega}{k_BT}\right] \tag{6}$$

Internal Energy (E=F+TS)

$$E = Nk_BT \tag{7}$$

This result is in accordance with law of equipartition of energy, according to which each quadratic term in the Hamiltonian for each harmonic oscillator contributes a term $\frac{1}{2}k_BT$.

Pressure (P)

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N,T} = 0 \tag{8}$$

Chemical Potential (μ)

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = Nk_BT\ln\frac{\hbar\omega}{k_BT} \tag{9}$$

Specific heat ($C_p = C_V$)

$$C_P = C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = k_BT \tag{10}$$

(b) Quantum mechanical approach

Quantum mechanically, each linear harmonic oscillator is characterized by energy eigen value given by

$$\epsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega\ , n = 0,1,2,3\ \ldots\ldots\ldots\ldots \tag{11}$$

Once again single oscillator partition function can be written as

$$z_1 = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n} = e^{-\left(\frac{1}{2}\beta\hbar\omega\right)}\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = \frac{e^{-\left(\frac{1}{2}\beta\hbar\omega\right)}}{1-e^{-\beta n\hbar\omega}} \tag{12}$$

$$= \left[2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right]^{-1}$$

The partition function for the N Oscillator system is given by

$$Z = (Z_1)^N \; = \; \left[2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right]^{-N} \tag{13}$$

Now we can derive all thermodynamic properties

Helmholtz free energy (F)

$$\begin{aligned} F &= -k_B T \ln Z = N k_B T \ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right] \\ &= N\left[\frac{1}{2}\hbar\omega + k_B T \ln\left(1 - e^{-\beta\hbar\omega}\right)\right] \end{aligned} \tag{14}$$

Entropy (S)

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_{N,V} \\ &= N k_B\left\{\left[\frac{1}{2}\beta\hbar\omega \coth\left(\frac{1}{2}\beta\hbar\omega\right)\right] - \ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right]\right\} \end{aligned} \tag{15}$$

Internal Energy ($E = F + TS$)

$$E = F + TS = \frac{1}{2}N\hbar\omega \; \coth\left(\frac{1}{2}\beta\hbar\omega\right) = \; N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\left(e^{\beta\hbar\omega} - 1\right)}\right] \tag{16}$$

This result is in not in accordance with law of equipartition of energy, according to which each quadratic term in the Hamiltonian for each harmonic oscillator contributes a term $\frac{1}{2}k_B T$.

Pressure (P)

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N,T} = 0 \tag{17}$$

Chemical Potential (μ)

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left[\frac{1}{2}\hbar\omega + k_B T \ln\left(1 - e^{-\beta\hbar\omega}\right)\right] \tag{18}$$

Specific heat ($C_p = C_V$)

$$C_P = C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = Nk_B\left(\frac{1}{2}\hbar\omega\beta\right)^2 \operatorname{cosech}^2\left(\frac{1}{2}\beta\hbar\omega\right) \qquad (19)$$

$$= Nk_B(\hbar\omega\beta)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

All these results from (5) to (9) approach classical results for $k_BT \gg \hbar\omega$

3.1 Paramagnetism

Let us now examine a collection of N independent identical spins sitting at different points using partition function approach. Each of these spins can be treated as magnetic dipoles with a magnetic moment μ. These are distinguishable as they are sitting at different locations. These form a non-interacting system in the sense that each magnetic dipole does not experience the field of the other dipoles. These magnetic dipoles can be orientedin any direction with the application of external magnetic field. Since the spins are localized they have no kinetic energy. The Hamiltonian of such a system consists, therefore, of magnetic potential energy in the presence of magnetic field $\vec{\mathrm{H}}$only which can be written as

$$H = -\sum_{i=1}^{N}\vec{\mu_i}\,.\,\vec{\mathrm{H}} \qquad (20)$$

Here μ_i is the magnetic moment of the ith magnetic dipole.

We look at the system both classically and quantum mechanically and try to get some well-knownresult such as Curie Law for paramagnetic systems.

(i) A classical Treatment

In this case equation (20) can be written explicitly in terms of orientation θ_i of each magnetic dipole as

$$H = -\sum_{i=1}^{N}\mu_i\,\mathrm{H}\cos\theta_i = -N\mu\mathrm{H}\sum_{\theta}\cos\theta \qquad (21)$$

Now the single particle partition function can be written, remembering that three dimensional orientation is decided by θ and ϕ

So that single dipole partition function can be written as

$$Z_1 = \sum_{\theta} e^{(\beta\mu \mathrm{H} \cos\theta)} = \int_0^{2\pi}\int_0^{\pi} e^{(\beta\mu \mathrm{H}\cos\theta)} \sin\theta \, d\theta d\phi \tag{22}$$

Putting $\mathbf{x} = \cos\theta$ we solve equation (22) to get

$$Z_1 = \int_0^{2\pi}\int_{-1}^{+1} e^{(\beta\mu \mathrm{H}\, x)} dx d\phi = 4\pi \frac{\sinh(\beta\mu\,\mathrm{H})}{(\beta\mu\mathrm{H})} \tag{23}$$

So the partition function of the system can be written as

$$Z = (Z_1)^N = \left(4\pi \frac{\sinh(\beta\mu\,\mathrm{H})}{(\beta\mu\mathrm{H})}\right)^N \tag{24}$$

Now we can calculate the thermodynamic properties using the results derived in module XIII.

Helmholtz free energy (F)

$$F = -N\,\mathrm{k_B T}\ln\left(4\pi \frac{\sinh(\beta\mu\,\mathrm{H})}{(\beta\mu\mathrm{H})}\right) \tag{25}$$

Magnetization M of the system

$$M = -\left(\frac{\partial F}{\partial \mathrm{H}}\right)_{T,N} = N\mathrm{k_B T}\frac{\partial(\ln(\sinh(\beta\mu\,\mathrm{H})) - \ln(\beta\mu\mathrm{H}))}{\partial\mathrm{H}} = \tag{26}$$

$$M = N\,\mu\left\{\coth\beta\mu\mathrm{H} - \frac{1}{\beta\mu\mathrm{H}}\right\} = N\mu L(\beta\mu\mathrm{H}) \tag{27}$$

The mean magnetization in the direction of the magnetic field is

$$\langle\mu\rangle = \frac{M}{N} = \mu\left\{\coth\beta\mu\mathrm{H} - \frac{1}{\beta\mu\mathrm{H}}\right\} \tag{28}$$

Where $L(x) = \left\{\coth x - \frac{1}{\mathrm{x}}\right\}$is the Langevin function, here $x = \beta\mu\mathrm{H}$ is a parameter giving the ratio of magnetic potential energy $(\mu\mathrm{H})$ to thermal energy $(k_B T)$..

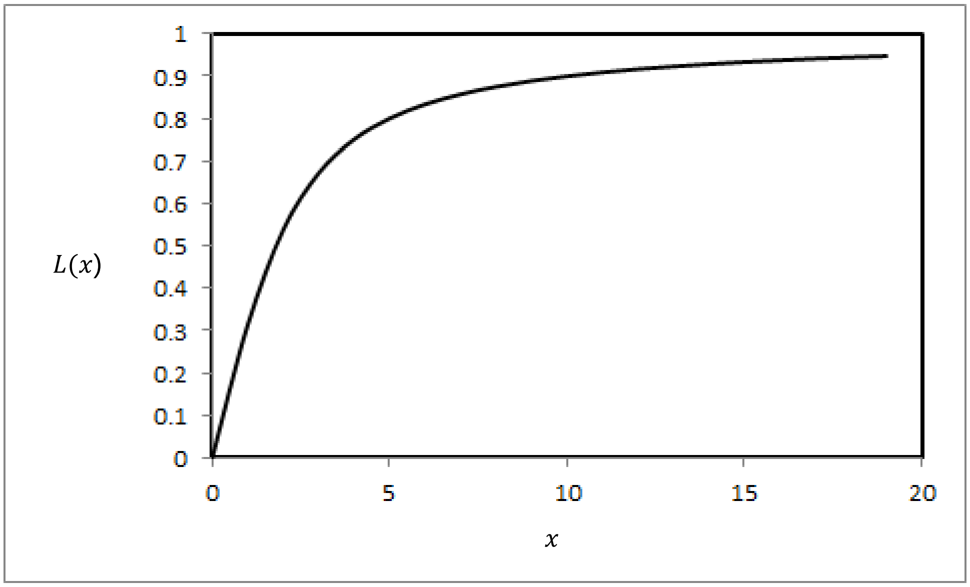

Figure 1Langevin Function

There are two limiting cases which provide us interesting results

(i) Low temperature or High magnetic field limit ($\boldsymbol{\mu}\mathbf{H} \gg \boldsymbol{k_B T}$):

In this limit Langevin function saturates to 1, figure 1, i.e all magnetic dipoles align in the direction of magnetic field and the net magnetization shall be

$$\boldsymbol{M} = \boldsymbol{N}\,\boldsymbol{\mu} \tag{29}$$

(ii) High temperature or Low magnetic field limit ($\boldsymbol{\mu}\mathbf{H} \ll \boldsymbol{k_B T}$):

In this limit $\mathbf{coth}\,\boldsymbol{x} = \frac{\mathbf{1}}{\boldsymbol{x}} + \frac{\boldsymbol{x}}{\mathbf{3}} - \frac{\boldsymbol{x}^{\mathbf{3}}}{\mathbf{45}} + \cdots$ and the Langevin function $\boldsymbol{L}(\boldsymbol{x}) \approx \boldsymbol{x}/\mathbf{3}$

Therefore,

$$\boldsymbol{M} = \boldsymbol{N}\frac{\boldsymbol{\mu}^{\mathbf{2}}\mathbf{H}}{\mathbf{k_B}\boldsymbol{T}} \tag{30}$$

In this limit susceptibility $\boldsymbol{\chi} = \frac{\partial \boldsymbol{M}}{\partial \boldsymbol{H}}$ becomes

$$\boldsymbol{\chi} = \frac{\partial \boldsymbol{M}}{\partial \boldsymbol{H}} = \frac{\boldsymbol{N}\boldsymbol{\mu}^{\mathbf{2}}}{\mathbf{k_B}\boldsymbol{T}} = \frac{\boldsymbol{C}}{\boldsymbol{T}} \tag{31}$$

This is famous Curie Law of para-magnetism which was experimentally verified to be true for copper-potassium sulphate hexahydrate.

(i) A Quantum Mechanical treatment.

To treat the problem of para-magnetism quantum mechanically, we must note that (i) magnetic moment of the particle involved of the system depends on its angular momentum $\vec{J}$(ii) magnetic moment $\vec{\mu}$and its component in the direction of magnetic field does not have arbitrary values but are discrete.

If angular momentum of the system is $\vec{J}$ its magnetic moment $\vec{\mu}$ is given by

$$\vec{\mu} = \mu_B g\vec{J} \tag{32}$$

Where $\mu_B = \frac{e\hbar}{2mc}$ is Bohr magneton and g is Lande factor given by

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \tag{33}$$

If the particles involved are electrons i.e. $S = 1/2$ with $L = 0$ the total angular momentum $J = \frac{1}{2}$, $g = 2$. On the other hand if $S = 0$ then g is solely due to L and $g = 1$.

Now if we take magnetic field in the direction ofz-axis the component of $\vec{\mu}$ in this direction μ_z is given by:

$$\mu_z = g\mu_B m, m = -J, -J+1, \dots, J-1, J \tag{34}$$

Now we are in a position to write down the single partition function in the presence of magnetic field:

$$Z_1 = \sum_{m=-J}^{m=+J} e^{g\mu_B m \mathrm{H}\beta} \tag{35}$$

The sum in equation (17) is a geometrical progression with $(2J+1)$ terms with first term $e^{-g\mu_B \mathrm{JH}\beta}$ and common ratio $e^{g\mu_B \mathrm{H}\beta}$, therefore, Z_1 is given by

$$Z_1 = \frac{e^{-g\mu_B J \mathrm{H}\beta}\left(1 - e^{g\mu_B \mathrm{H}\beta(2J+1)}\right)}{1 - e^{g\mu_B \mathrm{H}\beta}} \tag{36}$$

This can be further simplified to give

$$\boldsymbol{Z_1} = \frac{\left(e^{-g\mu_B \mathrm{H}\beta\left(J+\frac{1}{2}\right)} - e^{g\mu_B \mathrm{H}\beta\left(j+\frac{1}{2}\right)}\right)}{\left(e^{-\frac{g\mu_B \mathrm{H}\beta}{2}} - e^{\frac{g\mu_B \mathrm{H}\beta}{2}}\right)} = \frac{\sinh g\mu_B \mathrm{Hj}\beta\left(1+\frac{1}{2J}\right)}{\sinh \frac{g\mu_B \mathrm{H}J\beta}{2J}} \tag{37}$$

Putting $g\mu_B\mathrm{Hj}\beta = x$, equation (36) becomes

$$\boldsymbol{Z_1} = = \frac{\sinh x\left(1+\frac{1}{2J}\right)}{\sinh \frac{x}{2J}} \tag{38}$$

So the total partition function of the system is given by

$$\boldsymbol{Z} = \left(\frac{\sinh x\left(1+\frac{1}{2J}\right)}{\sinh \frac{x}{2J}}\right)^{N} \tag{39}$$

Now we will be in a position to calculate thermodynamic properties of the system.

Helmholtz Free Energy($\boldsymbol{F}$):

$$\boldsymbol{F} = -Nk_BT\left[\ln\sinh\left(g\mu_B\mathrm{Hj}\beta\left(1+\frac{1}{2\mathrm{J}}\right)\right) - \ln\sinh\left(\frac{g\mu_B\mathrm{Hj}\beta}{2\mathrm{J}}\right)\right] \tag{40}$$

Magnetization $\boldsymbol{M}$: Since $\boldsymbol{M} = -\left(\frac{\partial F}{\partial \mathrm{H}}\right)_{T,N}$

$$\boldsymbol{M} = N\,g\mu_B J\left[\left(1+\frac{1}{2J}\right)\coth\left\{g\mu_B\mathrm{H}J\beta\left(1+\frac{1}{2\mathrm{J}}\right)\right\} - \left(\frac{1}{2J}\right)\coth\left\{\frac{g\mu_B\mathrm{H}J\beta}{2J}\right\}\right] \tag{41}$$

Or

$$\boldsymbol{M} = Ng\mu_B J\,B_J(g\mu_B\mathrm{H}J\beta) \tag{42}$$

Where $B_J(g\mu_B\mathrm{H}J\beta)$ is a Brillouin function of order J, where J is the relevant quantum number. The plot of the Brillouin function is given in Figure 2 below:

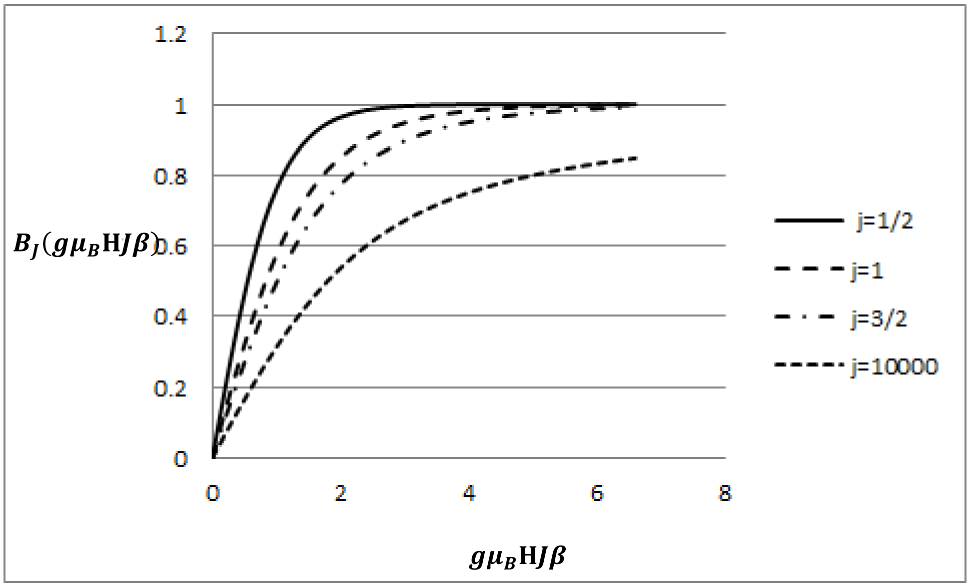

Figure 2 Brillouin function for sample values of $\boldsymbol{J}$

From Figure 2, it is clear that large values of $\boldsymbol{g\mu_B \mathrm{H} J\beta \gg 1}$ i.e for strong field and low temperature, the Brillouin function approaches 1 for all values of $\boldsymbol{J}$, showing state of magnetic saturation. However, for $\boldsymbol{g\mu_B \mathrm{H} J \ll 1}$ i.e.weak field and high temperature, the Brillouin function, knowing that $\boldsymbol{\coth x \cong \frac{1}{x} + \frac{x}{3}}$ for $\boldsymbol{x \ll 1}$ so that Brillouin function can be written as

$$B_J(x) \cong \left(1 + \frac{1}{2J}\right)\left(\frac{1}{\left\{g\mu_B \mathrm{H} J\beta\left(1 + \frac{1}{2\mathrm{J}}\right)\right\}} + \frac{\left\{g\mu_B \mathrm{H} J\beta\left(1 + \frac{1}{2\mathrm{J}}\right)\right\}}{3}\right) - \left(\frac{1}{2J}\right)\left(\frac{1}{\left\{\frac{g\mu_B \mathrm{H} J\beta}{2j}\right\}} + \frac{\left\{g\mu_B \mathrm{H} J\beta\left(\frac{1}{2\mathrm{J}}\right)\right\}}{3}\right) \tag{43}$$

Or

$$B_J(x) \cong \frac{g\mu_B \mathrm{H} J\beta}{3}\left[\left(1 + \frac{1}{2J}\right)^2 - \left(\frac{1}{2J}\right)^2\right] = \frac{g\mu_B \mathrm{H} J\beta}{3}\left[1 + \frac{1}{J}\right] \tag{44}$$

Therefore,

$$\boldsymbol{M} = \frac{N(g\mu_B)^2 J(J+1)}{3k_B T}\mathbf{H} \tag{45}$$

Once again we get Curie Law:

$$\chi = \left(\frac{\partial M}{\partial H}\right) = \frac{N(g\mu_B)^2 J(J+1)}{3k_B T} = \frac{C}{T} \tag{46}$$

Where, now $C = \frac{N(g\mu_B)^2 J(J+1)}{3k_B} = \frac{N\mu^2}{3k_B}$with $\mu^2 = (g\mu_B)^2 J(J+1)$, a departure from classical result.

In the limit $J \to \infty$, Brillouin function reduces toLangevin function:

$$\left(1+\frac{1}{2J}\right)\coth\left\{x\left(1+\frac{1}{2J}\right)\right\} - \left(\frac{1}{2J}\right)\coth\left\{\frac{x}{2J}\right\} \to \coth\{x\} - \frac{\left(\frac{1}{2J}\right)2j}{x} = \coth x - \frac{1}{x}$$

This is expected, $J \to \infty$ amounts to saying that there are tremendously large orientations in which the magnetic dipoles can align, this situation is the same as in the classical case and should yield the classical result.

4. Equipartition Theorem

Equipartition theorem also known as law of equipartition of energy is a classical theorem. According to it in classical limiting case every canonical variable (generalized position and momentum) entering quadratically or harmonically in a Hamiltonian function(Energy) has a mean thermal energy $\frac{k_B T}{2}$. For example, Hamiltonian function in three dimensions may be written as

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2 + \frac{1}{2}\frac{L^2}{I} + \frac{(E^2 + B^2)}{8\pi} \tag{47}$$

This Hamiltonian represents energy possessed by a molecule which is respectively made up of translational kinetic energy, harmonic potential energy, rotational kinetic energy and electromagnetic energy in an electromagnetic field. Each term is quadratic in one of the canonical variables. Therefore, according to law of equipartition of energy, in three dimensions.Thus thermal energy E is given by $\frac{3k_B T}{2} + \frac{3k_B T}{2} + k_B T + 2k_B T$, here we have three canonical variables for translational motion, three for vibrational motion, two for rotational motion and two each for electrical energy and magnetic energy. This theorem can be proved easily using canonical distribution function. In this section we prove this result with a slightly sophisticated approach.

Proof: Suppose we have a classical system of N particles with $6N$ generalized coordinates (q_i, p_i), where i goes from 1 to $3N$, giving a total of $6N$ coordinates. We are interested in calculating the mean value of the quantity $x_i \frac{\partial H}{\partial x_j}$, where $x_i$and x_j are any of the $6N$ coordinates. In canonical ensemble it is given by:

$$\langle x_i \frac{\partial H}{\partial x_j}\rangle = \frac{\int e^{-\beta H(q,p)}\left(x_i \frac{\partial H}{\partial x_j}\right) d\omega}{\int e^{-\beta H(q,p)} d\omega} \tag{48}$$

Where $d\omega = d^{3N}q\, d^{3N}\mathbf{p}$. Out of $d\omega$ let us pick up integration over x_j in the numerator and do this integration by parts. First we note that $e^{-\beta H(q,p)}\left(x_i \frac{\partial H}{\partial x_j}\right) = -\frac{1}{\beta} x_i \frac{\partial e^{-\beta H(q,p)}}{\partial x_j}$ so equation (48) can be written as

$$\langle x_i \frac{\partial H}{\partial x_j}\rangle = -\frac{1}{\beta}\frac{\int x_i \frac{\partial e^{-\beta H(q,p)}}{\partial x_j}\, dx_j \mathbf{d\omega}_{remaing\ co-ordinates}}{\int e^{-\beta H(q,p)} d\omega} \tag{49}$$

So integral over x_j becomes

$$\int x_i \frac{\partial e^{-\beta H(q,p)}}{\partial x_j}\, dx_j = x_i\, e^{-\beta H(q,p)}\Big|_{x_{j1}}^{x_{j2}} - \int \frac{\partial x_i}{\partial x_j}\, e^{-\beta H(q,p)}\, dx_j \tag{50}$$

To take limits over the first term we note that there are two possibilities:

(i) If x_j are momentum co-ordinates, the kinetic energy tends to infinity at extremely large values, making Hamiltonian infinite and $e^{-\beta H(q,p)} \rightarrow \mathbf{0}$.

(ii) If x_j happens to be position co-ordinates, the limits mean on the walls of the container in which system is enclosed, where potential energy is infinite and once again Hamiltonian becomes infinite leading to $e^{-\beta H(q,p)} \rightarrow \mathbf{0}$.

Thus we can conclude that first term vanishes. So equation (50) becomes

$$\begin{aligned}\int x_i \frac{\partial e^{-\beta H(q,p)}}{\partial x_j}\, dx_j &= -\int \frac{\partial x_i}{\partial x_j}\, e^{-\beta H(q,p)}\, dx_j \\ &= -\int \delta_{ij}\, e^{-\beta H(q,p)}\, dx_j\end{aligned} \tag{51}$$

Hence equation (49) can be written as

$$\begin{aligned}\langle x_i \frac{\partial H}{\partial x_j}\rangle &= \frac{1}{\beta}\frac{\int \delta_{ij}\, e^{-\beta H(q,p)}\, dx_j \mathbf{d\omega}_{remaing\ co-ordinates}}{\int e^{-\beta H(q,p)} d\omega} \\ &= \frac{\delta_{ij}}{\beta}\frac{\int e^{-\beta H(q,p)}\mathbf{d\omega}}{\int e^{-\beta H(q,p)} d\omega} = \frac{\delta_{ij}}{\beta} = \delta_{ij} k_B T\end{aligned} \tag{52}$$

This is an extremely general result and is independent of the precise form of the $H(q,p)$.

From equation (52) the following results follow immediately:

If $x_i = x_j = p_i$	$\langle p_i \frac{\partial H}{\partial p_j}\rangle = k_B T$	$\sum_{i=1}^{3N} \langle p_i \frac{\partial H}{\partial p_j}\rangle = 3Nk_B T$
If $x_i = x_j = q_i$	$\langle q_i \frac{\partial H}{\partial q}\rangle = k_B T$	$\sum \langle q_i \frac{\partial H}{\partial q_i}\rangle = 3Nk_B T$

What about the statement of the law of equipartion of energy made earlier *that every canonical variable (generalized position and momentum) entering quadratically or harmonically in a Hamiltonian function(Energy) has a mean thermal energy*$\frac{k_B T}{2}$

This can be checked easily. Let us take a Hamiltonian which is is a quadratic function of co-ordinates, by suitable canonical transformation, it can be converted into a form:

$$H = \sum_i A_j P_j^2 + \sum_i B_j Q_j^2 \tag{53}$$

Where, $Q_j$and P_j are canonically conjugate transformed coordinates and A_j and B_j are suitable constants.

Then it immediately follows that

$$\sum_j \left(P_j \frac{\partial H}{\partial p_j} + Q_j \frac{\partial H}{\partial q_j} \right) = 2H \tag{54}$$

Therefore, from the table it follows that

$$\langle H \rangle = \frac{1}{2} \sum_j \left(\langle P_j \frac{\partial H}{\partial P_j}\rangle + \langle Q_j \frac{\partial H}{\partial Q_j}\rangle \right) = \frac{1}{2}(6Nk_B T) = \frac{1}{2} f k_B T \tag{55}$$

Here 6N are the number of degrees of freedom corresponding to number of non-zero coefficients in the transformed Hamiltonian (53). One can immediately conclude that corresponding to each quadratic term in the Hamiltonian there is a contribution of $\frac{1}{2}k_B T$, proving the statement providing an alternative proof for the equipartition theorem.

Applications of law of equipartition:

Law of equipartition theorem provides a back of the stamp method to calculate in classical regime (i.e. at sufficiently high temperature and low density) to calculate internal energy and specific heat. Quantum mechanically a system has discrete energy levels, however at sufficiently high temperatures, the spacing ΔE between energy levels is $\ll k_B T$. One can then treat discrete energy level structure as a continuum and law of equipartition which is valid in classical regime can be applied. In the following we look at application of equipartition theorem in some well-known systems.

A monoatomic gas: Single atom in a monoatomic gas has only translational kinetic energy, so that total Hamiltonian of the 1mole monoatomic system can be written as $\sum_{i=1}^{N}(\frac{p_{ix}^2}{2m}+\frac{p_{iy}^2}{2m}+\frac{p_{iz}^2}{2m})$, where N is Avagadro's number, so that there are $3N$ quadratic terms in momentum coordinate in it. According to law of equipartition of energy, the energy of this N particle monoatomic gas can be written as

$$E = 3N\frac{k_BT}{2} = \frac{3}{2}RT \tag{56}$$

The molar specific heat at constant volume $C_v = \frac{3}{2}R$. Using $C_p - C_v = R$, specific heat at constant pressure is then given by $C_p = \frac{5}{2}R$. The ratio of the two specific heats $\gamma = \frac{C_p}{C_v} = \frac{5}{3}$, a well-known result.

A diatomic gas: Each particle of the gas in thios case is made up of a diatomic molecule, which can be assumed to be a dumb bell shaped rigid rotator, with arotational symmetry about the line joining the nuclei of the two atoms along Z-axis. So the Hamiltonian of the diatomic molecule has three translational kinetic energy terms quadratic in three components of the linear momentum and two terms corresponding to rotational kinetic energy quadratic in $\sum_{i=1}^{N}\left[\left(\frac{p_{ix}^2}{2m}+\frac{p_{iy}^2}{2m}+\frac{p_{iz}^2}{2m}\right)+\left(\frac{J_{ix}^2}{2I}+\frac{J_{iy}^2}{2I}\right)\right]$where J is angular momentum and I moment of inertia. Hamiltonian thus has 5N quadratic terms.According to law of equipartition of energy the energy of this N diatomic molecule system can be written as

$$E = \frac{5}{2}Nk_BT = \frac{5}{2}RT \tag{57}$$

Where N is Avagadro's number.

The molar specific heat at constant volume $C_v = \frac{5}{2}R$. Using $C_p - C_v = R$, specific heat at constant pressure is then given by $C_p = \frac{7}{2}R$. The ratio of the two specific heats ($\gamma = \frac{C_p}{C_v} = \frac{7}{5}$, a well-known result which agree very nicely with experimental results at room temperature. It must be mentioned here that if we relax the condition of rigid molecule in this discussion we expect molecule to vibrate as a one dimensional harmonic oscillator having energy which is partly kinetic and partly kinetic contributing two additional terms so that each molecule contributes vibrational kinetic energy of $2 \times \frac{1}{2}k_BT$, so that

$$E = \frac{5}{2}Nk_BT + N\,k_BT = \frac{7}{2}RT \tag{58}$$

So that $C_V = \frac{7}{2}R$, $C_p = \frac{9}{2}R$ and $\gamma = \frac{9}{7}$. The observed values do not agree with experiments indicating that at room temperature diatomic molecule has no vibrational motion. The vibrations get excited only in the case of high temperature limit.

A crystalline solid:

A simple model of crystalline solid consists of a collection of atoms, with each lattice having one atom, where it can not move or rotate but can behave as an independent harmonic oscillator. Each oscillator having 6 quadratic terms three for kinetic energy and three for potential energy: $\left[\left(\frac{p_{ix}^2}{2m} + \frac{p_{iy}^2}{2m} + \frac{p_{iz}^2}{2m}\right) + \left(\frac{1}{2}K(q_{ix}^2 + q_{iy}^2 + q_{iz}^2)\right)\right]$. So according to law of equipartition energy, we have energy of one mole of a solid:

$$E = 6N\frac{1}{2}k_BT = 3\ RT \tag{59}$$

Thus molar specific heat of a solid at constant volume $C_v = 3R$, well-known Dulong and Petit's law. This is found to be the case at high temperature, but is not true at low temperatures and we need to go beyond classical law of equipartition of energy and quantum mechanics invoked as was done by Einstein.

5. Virial Theorem:

In classical mechanics the products $p_i\frac{\partial H}{\partial p_i} = p_i\dot{q}_i$ and $q_i\frac{\partial H}{\partial q_i} = -q_i\dot{p}_i$ have a special significance. The second expression which is a product of position coordinate and generalized force is called virial and when summed over all i its mean value gives virial theorem of statistical mechanics:

$$\mathcal{V}_{id} = \left\langle\sum_{i=1}^{3N} q_i\dot{p}_i\right\rangle = -\left\langle\sum_{i=1}^{3N} q_i\frac{\partial H}{\partial q_i}\right\rangle = -3Nk_BT \tag{60}$$

Virial has a very interesting relationship with the physical quantities of a system and starting from it equation of state can be derived. Let us take the case of an ideal gas. It is enclosed in a container and walls provide the only external force to keep the gas confinedin the form of external pressure P. So here we have a forse $-P\overrightarrow{dS}$ on an area element $\overrightarrow{dS}$ of the wall. The virial of the ideal gas can be calculated as:

$$\mathcal{V}_{id} = \sum_{i=1}^{3N} q_i\dot{p}_i = \sum_{i=1}^{3N} q_iF_i = -P\oint_s \vec{r}.\overrightarrow{ds} \tag{61}$$

Where $\vec{r}$ is the position vector corresponding to the surface element with a particle in its vicinity. Using divergence theorem we have

$$\mathcal{V}_{id} = -P \oint_V \vec{\nabla}.\vec{r}\, dV = -3PV \tag{62}$$

Applying Virial Theorem, we have ideal equation of state:

$$PV = NKT \tag{63}$$

Furthermore, Kinetic energy of an ideal gas say $E_k = \frac{3}{2}Nk_bT = -\frac{\mathcal{V}_{id}}{2}$, therefore,

$$\mathcal{V}_{id} = -2E_k \tag{64}$$

Virial has many interesting applications where it can from the knowledge of two particle potential be used to calculate the equation of state of the system, which becomes very useful in calculation of pressure computationally.

6. Density of State over Energy:

We have till this point focused on the number of microstates in a region of phase space and arrived at a result that for a system with f degrees of freedom, a volume $(2\pi\hbar)^f$ in the phase space contains one microstate. However, in many practical situations, e.g. in condensed matter physics we are interested in finding the number of states which are available to it in a small energy interval $\epsilon$and $\epsilon + d\epsilon$. This important number can be obtained if we know relation between energy (ϵ) and momentum (p), also called dispersion relation. These relations for a free particle system for non-relativistic, ultra relativistic (mass neglected or mass less particles) and relativistic particles are given in the table below:

Table 1 Dispersion relation for a free particle system

System	Dispersion relation
Non-relativistic	$\epsilon = \frac{p^2}{2m}$
Relativistic	$\epsilon^2 = c^2p^2 + m^2C^4$
Ultra relativistic	$\epsilon = cp$

Let us derive for a three dimensional system, the density of states $\mathcal{D}(\epsilon)$, the number of states of a particle per unit volume per unit energy range about ϵ.

Let us begin by counting the number of states for a free particle in three dimensions in small region of phase space $\boldsymbol{d^3r\, d^3p}$, then since particle has three degrees of freedom we have

$$\text{Number of states in phase space volume}\boldsymbol{d^3r\, d^3p} = \frac{\boldsymbol{d^3rd^3p}}{\boldsymbol{(2\pi\hbar)^3}} \tag{65}$$

.

If the particles have some internal degrees of freedom, let us denote this by $\boldsymbol{g}$ then the abover relation becomes

$$\text{Number of states in phase space volume}\boldsymbol{d^3r\, d^3p} = \boldsymbol{g}\,\frac{\boldsymbol{d^3rd^3p}}{\boldsymbol{(2\pi\hbar)^3}} \tag{66}$$

Let us assume that system is homogeneous, then this number is independent of the position of the phase space volume element. Then we can integrate over the postion coordinates to obtain

$$\text{Number of states in momentum space volume}\boldsymbol{d^3p} = \boldsymbol{g}\,\frac{\boldsymbol{Vd^3p}}{\boldsymbol{(2\pi\hbar)^3}} \tag{67}$$

Now if we take system to be isotropic, this number depends only on the magnitude of momentum $\vec{\boldsymbol{p}}$, we can then integrate over angular variables $\boldsymbol{\theta}$ and $\boldsymbol{\phi}$, so that we get

$$\text{Number of states between } \boldsymbol{p} \text{ and } \boldsymbol{p+dp} = \boldsymbol{g}\,\frac{\boldsymbol{4\pi Vp^2dp}}{\boldsymbol{(2\pi\hbar)^3}} \tag{68}$$

Now let $\boldsymbol{\mathcal{D}(\epsilon)}$ be the number of states of a particle per unit volume per unit energy range about $\boldsymbol{\epsilon}$ then

$$\boldsymbol{V\mathcal{D}(\epsilon)d\epsilon = g\,\frac{4\pi Vp^2dp}{(2\pi\hbar)^3}} \tag{69}$$

Or

$$\boldsymbol{\mathcal{D}(\epsilon) = g\,\frac{4\pi\, p^2}{(2\pi\hbar)^3}\frac{dp}{d\epsilon}} \tag{70}$$

Now by using dispersion relations given in Table 1, we can get density of states for each of the cases for a three dimensional system as given in Table 2 below

Table 2 Density of states over energy for a three dimensional system

System	Dispersion relation	$\frac{dp}{d\epsilon}$	$\mathcal{D}(\epsilon)$
Non-relativistic	$\epsilon = \frac{p^2}{2m}$	$(2m^3\epsilon)^{-\frac{1}{2}}$	$\frac{g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}$
Relativistic	$\epsilon^2 = c^2p^2 + m^2c^4$	$\frac{2\epsilon}{C}(\epsilon^2 - m^2c^4)^{-\frac{1}{2}}$	$\frac{g}{2\pi^2}\frac{\epsilon(\epsilon^2 - m^2c^4)^{\frac{1}{2}}}{(c\hbar)^3}$
Ultra relativistic	$\epsilon = cp$	$\frac{1}{c}$	$\frac{g}{2\pi^2}\frac{\epsilon^2}{(\hbar c)^3}$

Similarly density of states for two dimensional systems, one dimensional systems and zero dimensional systems can be obtained.

7. Summary

In this module we have learnt

- How the properties from the knowledge of patition function of the following systems their thermodynamic properties can be obtained:

i. *A system of harmonic oscillators:* $\boldsymbol{H = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} + \frac{1}{2}m\omega^2 q_i^2\right)}$

Physical Quantity	Classical approach	Quantum Approach
Partition function	$Z = Z_1^N = (\beta\hbar\omega)^{-N}$	$Z = \left[2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right]^{-N}$
Helmholtz free energy	$F = Nk_BT\ln\frac{\hbar\omega}{k_BT}$	$F = N\left[\frac{1}{2}\hbar\omega + k_BT\ln(1 - e^{-\beta\hbar\omega})\right]$
Entropy	$S = Nk_B\left[1 - \ln\frac{\hbar\omega}{k_BT}\right]$	$S = Nk_B\left\{\left[\frac{1}{2}\beta\hbar\omega\coth\left(\frac{1}{2}\beta\hbar\omega\right)\right] - \ln\left[2\sinh\left(\frac{1}{2}\beta\hbar\omega\right)\right]\right\}$
Internal Energy	$E = Nk_BT$	$E = \frac{1}{2}N\hbar\omega\ \coth\left(\frac{1}{2}\beta\hbar\omega\right) =$
Pressure	$P = 0$	$P = 0$
Chemical potential	$\mu = Nk_BT\ln\frac{\hbar\omega}{k_BT}$	$\mu = \left[\frac{1}{2}\hbar\omega + k_BT\ln(1 - e^{-\beta\hbar\omega})\right]$
Specific heat	$C_P = C_V = k_BT$	$C_P = C_V = Nk_B(\hbar\omega\beta)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$

In the classical limit $\frac{\hbar\omega}{k_BT} \ll \mathbf{1}$ all quantum mechanical results approach classical results.

ii. *Para-magnetism (Classical and Quantum Mechanical Treatment)*

The Hamiltonian for a classical system of magnetic dipoles in a magnetic field is given by

$$H = -\sum_{i=1}^{N} \vec{\mu_i} . \vec{\mathrm{H}} = -\sum_{i=1}^{N} \mu_i \,\mathrm{H} \cos\theta_i = -N\mu\mathrm{H} \sum_{\theta} \cos\theta$$

Physical Quantity	Classical approach	Quantum Approach
Partition function	$Z = = \left(4\pi \frac{\sinh(\beta\mu\,\mathrm{H})}{(\beta\mu\mathrm{H})}\right)^N$	$Z = \left(\frac{\sinh x\left(1+\frac{1}{2J}\right)}{\sinh\frac{x}{2J}}\right)^N$ $where\ x = g\mu_B\mathrm{H}j\beta$
Helmholtz free energy	$F = -N\,\mathrm{k_B T}\ln\left(4\pi\frac{\sinh(\beta\mu\,\mathrm{H})}{(\beta\mu\mathrm{H})}\right)$	$F = -Nk_BT\left[\ln\sinh\left(x\left(1+\frac{1}{2\mathrm{J}}\right)\right) - \ln\sinh\left(\frac{x}{2\mathrm{J}}\right)\right]$
Magnetization	$M = -\left(\frac{\partial F}{\partial \mathrm{H}}\right)_{T,N} = N\mu\left\{\coth\beta\mu\mathrm{H} - \frac{1}{\beta\mu\mathrm{H}}\right\} = N\mu L(\beta\mu\mathrm{H})$	$M = N g\mu_B J\left[\left(1+\frac{1}{2J}\right)\coth\left\{g\mu_B\mathrm{H}J\beta\left(1+\frac{1}{2\mathrm{J}}\right)\right\} - \left(\frac{1}{2J}\right)\coth\left\{\frac{g\mu_B\mathrm{H}J\beta}{2J}\right\}\right] = Ng\mu_BJ\,B_J(g\mu_B\mathrm{H}J\beta)$
Magnetization in High magnetic field or low temperature limit	$M = N\mu$	$M = N g\mu_B J$
Magnetization in high temperature and low magnetic field limit	$M = N\frac{\mu^2\mathrm{H}}{\mathrm{k_B}T}$	$M = \frac{N(g\mu_B)^2 J(J+1)}{3k_BT}\mathrm{H}$
Susceptibility (in high temperature and low magnetic field limit)	$\chi = \frac{\partial M}{\partial H} = \frac{N\mu^2}{\mathrm{k_B}T} = \frac{C}{T}, C = \frac{N\mu^2}{\mathrm{k_B}}$	$\chi = \frac{N(g\mu_B)^2 J(J+1)}{3k_BT} = \frac{C}{T},$ $C = \frac{N(g\mu_B)^2 J(J+1)}{3k_B}$

- That law of equipartition theorem states that every canonical variable (generalized position and momentum) entering quadratically or harmonically in a Hamiltonian function(Energy) has a mean thermal energy $\frac{\mathrm{k_B T}}{2}$
- How to derive law of equipartition of energy in its most general form

$$\langle x_i \frac{\partial H}{\partial x_j}\rangle = \delta_{ij} k_B T$$

Where x_i and x_j are any of the $6N$ coordinates.

- How to apply law of equipartition of energy to get in the classical limit, internal energy E, molar specific heat at constant volume C_v, molar specific heat at constant pressure C_p and ratio of the specific heat γ for a monoatomic gas, for a diatomic gas (with and without vibrations) and a crystalline solid highlighting the limitations of the approach.
- How to calculate virial of an ideal gas,

$$\mathcal{V}_{id} = \langle \sum_{i=1}^{3N} q_i \dot{p}_i \rangle = -\langle \sum_{i=1}^{3N} q_i \frac{\partial H}{\partial q_i} \rangle = -3Nk_B T$$

And how it can we used to get equation of state of the ideal gas.

- How to calculate density of state over energy of a three dimensional gas of free particles
- That density of state over energy $\mathcal{D}(\epsilon) = g \frac{4\pi p^2}{(2\pi\hbar)^3} \frac{dp}{d\epsilon}$for non-relativistic, relativistic and ultra relativistic(mass less)gas is given by

System	$\mathcal{D}(\epsilon)$
Non-relativistic	$\frac{g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}$
Relativistic	$\frac{g}{2\pi^2} \frac{\epsilon(\epsilon^2 - m^2c^4)^{\frac{1}{2}}}{(c\hbar)^3}$
Ultra relativistic	$\frac{g}{2\pi^2} \frac{\epsilon^2}{(\hbar c)^3}$

Appendices

A1 Expansion of a logarithmic function and coth x

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots \text{for} x \ll 1.$$

$$\coth x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \cdots \text{for x<<1}$$

A2 Spreadsheet for plotting Langevinand Brillouin functions

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