

Lecture Notes - Week 9 (Lectures 24-26) ¹

Quantum Statistical Mechanics (Applications)

4.2 Harmonic Oscillators

4.2.1 Diatomic molecules

Recall that the heat capacity per molecule of an ideal gas is $C_V = \frac{3}{2}k_B$. However the measurements on many dilute gases do not agree with this. Monatomic gases like He do show this behaviour. However diatomic gases (like O₂ or CO) show a much more complicated behaviour. O₂ for example has $C_V = \frac{5}{2}k_B$ at room temperature which reduces to $C_V = \frac{3}{2}k_B$ below around 10K and increases to $C_V = \frac{7}{2}k_B$ for $T > 1000\text{K}$.

We would expect that a diatomic gas has a different (higher) heat capacity because it has more (internal) degrees of freedom (vibrations of the molecule and rotations). What is rather more puzzling is the complicated temperature dependence and the ‘disappearance’ of these degrees of freedom (d.o.f) at low temperatures.

Let us consider the effects of vibrations. A diatomic molecule has 1 vibrational mode (about its centre of mass) which we can model as a spring of stiffness K connecting two masses m_1, m_2 . The displacement of the spring from its equilibrium position is q and the associated conjugate momentum is p .

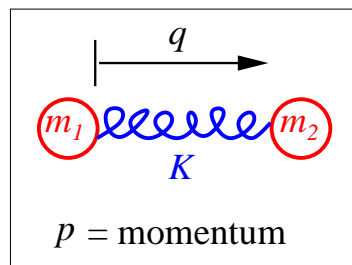


Figure 1: The vibration mode of a diatomic molecule measured by displacement q and conjugate momentum p .

The classical Hamiltonian of this system is the simple Harmonic Oscillator :

$$\mathcal{H}_{HO} = \frac{p^2}{2m} + \frac{Kq^2}{2} = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2} \quad (4.2.1)$$

where $m = \frac{m_1 m_2}{m_1 + m_2}$ and we have defined a frequency $\omega = \sqrt{\frac{K}{m}}$

The classical partition function is

$$Z_{HO}^c(T) = \int \frac{dpdq}{h} e^{-\beta \mathcal{H}_{HO}} = \frac{k_B T}{\hbar \omega} \quad , \quad \text{where} \quad \hbar = \frac{h}{(2\pi)} \quad (4.2.2)$$

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The internal energy and specific heat per molecule due to vibrations is then given by

$$E_{HO}^c = \langle \mathcal{H}_{HO} \rangle = -\frac{\partial \ln Z_{HO}^c}{\partial \beta} = k_B T \Rightarrow$$

$$C_{HO}^c = \frac{dE_{HO}^c}{dT} = k_B, \quad (4.2.3)$$

corresponding to an extra $\frac{1}{2}k_B T$ of energy per kinetic and potential energy degree of freedom (in agreement with the **equipartition theorem**). So as we expect there is an additional contribution to the specific heat from the internal d.o.f, however it is *T-independent*²! This means that including the rotational modes as well, we should expect $C_V = \frac{7}{2}k_B$ for all temperatures.

So the question is: Why do the experiments show that contributions from the vibrational and other modes vanish as $T \rightarrow 0$?

Let us try a quantum mechanical calculation for the vibrational modes.

The quantum Hamiltonian for the harmonic oscillator is

$$\hat{\mathcal{H}} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2 \hat{q}^2}{2} \quad (4.2.4)$$

We *can* solve this problem in a coordinate basis but it turns out to be rather long and cumbersome. There is a much more elegant method of solving it in the energy basis using the **ladder operator** method invented by Paul Dirac, Nobel Laureate and a former undergraduate (in applied mathematics) at Bristol University. It is also easily generalized to treat systems of many harmonic oscillators - a problem of fundamental importance in **quantum field theory**.

Let us define the operator, \hat{a} and its adjoint, \hat{a}^\dagger :

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{q} + \frac{i}{m\omega} \hat{p} \right) \quad (4.2.5)$$

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left(\hat{q} - \frac{i}{m\omega} \hat{p} \right). \quad (4.2.6)$$

Note that \hat{a} is not Hermitian since $\hat{a}^\dagger \neq \hat{a}$.

Now from the commutation relation of position and momentum $[\hat{q}, \hat{p}] = i\hbar$, it is straightforward to show from their definitions that the commutation relation of \hat{a}, \hat{a}^\dagger is

$$[\hat{a}, \hat{a}^\dagger] = 1. \quad (4.2.7)$$

From the definitions it also follows that the Hamiltonian can be written as

$$\hat{\mathcal{H}} = \hbar\omega \left(\hat{a}^\dagger \hat{a} + \frac{1}{2} \right). \quad (4.2.8)$$

Let $|\Phi\rangle$ be an energy eigenstate with energy E i.e. $\hat{\mathcal{H}}|\Phi\rangle = E|\Phi\rangle$. Consider the unnormalised state vector $|\Theta\rangle = \hat{a}|\Phi\rangle$; taking an inner product with itself

$$\langle \Theta | \Theta \rangle = \langle \Phi | \hat{a}^\dagger \hat{a} | \Phi \rangle \geq 0$$

²We would also expect another k_B from the 2-degrees of freedom associated with rotations.

$$\Rightarrow \langle \Phi | \frac{\hat{\mathcal{H}}}{\hbar\omega} - \frac{1}{2} | \Phi \rangle = \left(\frac{E}{\hbar\omega} - \frac{1}{2} \right) \geq 0 \Rightarrow E \geq \frac{1}{2}\hbar\omega \quad \text{minimum energy}$$

There is a ground state, $|\Phi_0\rangle$ with energy $E_0 = \frac{1}{2}\hbar\omega$ for which $\hat{a} |\Phi_0\rangle = 0$.

Simply applying the definitions and the commutation relations for \hat{a}, \hat{a}^\dagger shows that

$$[\hat{\mathcal{H}}, \hat{a}] = -\hbar\omega\hat{a} \quad ; \quad [\hat{\mathcal{H}}, \hat{a}^\dagger] = \hbar\omega\hat{a}^\dagger \quad (4.2.9)$$

Now consider acting on $\hat{a} |\Phi\rangle$ (for $|\Phi\rangle \neq |\Phi_0\rangle$) with the Hamiltonian operator :

$$\begin{aligned} \hat{\mathcal{H}} \hat{a} |\Phi\rangle &= \left([\hat{\mathcal{H}}, \hat{a}] + \hat{a} \hat{\mathcal{H}} \right) |\Phi\rangle = (-\hbar\omega\hat{a} + \hat{a}E) |\Phi\rangle \\ &= (E - \hbar\omega) \hat{a} |\Phi\rangle . \end{aligned} \quad (4.2.10)$$

Similarly we can show that

$$\hat{\mathcal{H}} \hat{a}^\dagger |\Phi\rangle = (E + \hbar\omega) \hat{a}^\dagger |\Phi\rangle . \quad (4.2.11)$$

Clearly then \hat{a} acts on an energy e-state with energy E to produce another energy e-state (after suitable normalisation) with energy $E - \hbar\omega$ ($\geq \hbar\omega/2$) and is called the **lowering operator**.

Similarly, \hat{a}^\dagger acts an energy e-state with energy E to produce another energy e-state (again after suitable normalisation) with energy $E + \hbar\omega$ and is called the **raising operator**.

So if we define $|0\rangle = |\Phi_0\rangle$, by acting successively on $|0\rangle$ with \hat{a}^\dagger (and multiplying by suitable normalisation factors, $|1\rangle = \frac{1}{\mathcal{N}_1} \hat{a}^\dagger |0\rangle$, $|2\rangle = \frac{1}{\mathcal{N}_2} (\hat{a}^\dagger)^2 |0\rangle$, ... with \mathcal{N}_n chosen s.t. $\langle n|n\rangle = 1$) we will be able to generate an infinite set of energy eigenstates $\{|0\rangle, |1\rangle, |2\rangle, \dots, |n\rangle, \dots\}$ such that

$$\hat{\mathcal{H}} |n\rangle = \mathcal{E}_n |n\rangle \quad , \quad \text{where} \quad \mathcal{E}_n = \hbar\omega \left(n + \frac{1}{2} \right) , \quad (4.2.12)$$

i.e. the energy levels are **quantized** (discrete) and not continuous as they are for the classical system.

Note also that $\hat{n} \equiv \hat{a}^\dagger \hat{a}$ is called the **number operator** and has eigenvalues $N = 0, 1, 2, \dots$ so that the Quantum H.O. Hamiltonian can also be written as

$$\hat{\mathcal{H}} = \hbar\omega \left(\hat{n} + \frac{1}{2} \right) . \quad (4.2.13)$$

Now we can perform the calculation of the quantum partition function

$$Z_{HO}^q(T) = \text{Tr}(e^{-\beta\hat{\mathcal{H}}}) = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \quad (4.2.14)$$

As $T \rightarrow \infty$ (high T limit),

$$\lim_{\beta \rightarrow 0} Z_{HO}^q = \frac{k_B T}{\hbar\omega} . \quad (4.2.15)$$

This is exactly the same as the classical calculation (but we needed to have used h as the measure of the classical phase space for this to happen). This is indeed quite general:

if we choose h as the measure of our classical phase-space (per particle) then quantum and classical calculations will coincide exactly at high T . This is sometimes referred to as **Weyl's law**.

Hence the internal energy is

$$E_{HO}^q(T) = \frac{1}{Z} \text{Tr}(\hat{\mathcal{H}} e^{-\beta\hat{\mathcal{H}}}) = -\frac{\partial \ln Z_{HO}^q}{\partial \beta} = \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}. \quad (4.2.16)$$

The temperature independent part of the internal energy, $\hbar\omega/2$ is called the **zero-point energy** and is due to *quantum fluctuations* which are present even at $T = 0$.

The specific heat per molecule is then

$$C_{HO}^q(T) = \frac{dE_{HO}^q}{dT} = k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}. \quad (4.2.17)$$

Looking at the limiting behaviour it is easy to see that as

$$T \rightarrow 0, \quad C_{HO}^q(T) \rightarrow 0 \quad (4.2.18)$$

$$T \rightarrow \infty, \quad C_{HO}^q(T) \rightarrow k_B \quad (4.2.19)$$

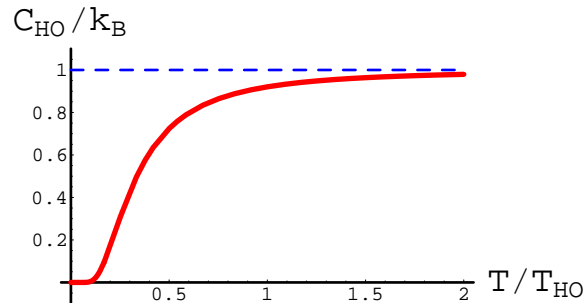


Figure 2: The specific heat/molecule, C_{HO}^q as a function of temperature.

There is a cross-over temperature $T_{HO} = \hbar\omega/k_B$ between the high and low T regimes. Using readily available estimates (Google!) for $\omega_{O_2} = \sqrt{K/m}$, we find that for O_2 , $T_{HO} \sim 1000$ K. Quantization of the vibrational modes is then the reason for the difference between $C_V = \frac{7}{2}k_B$ at v.high temperatures and $C_V = \frac{5}{2}k_B$ at room temperature. The drop to $C_V = \frac{3}{2}k_B$ at v.low T is due to the quantization of rotational motion.

4.2.2 Blackbody Radiation

This section is only for those doing M4500.

It has long been known that all bodies at finite T emit electromagnetic radiation (earlier experimental data was analysed by Stefan in 1879 and a thermodynamic explanation was put forward by Boltzmann 5 years later). These analyses showed that energy flux of emitted radiation depends upon temperature via the relationship known as the Stefan-Boltzmann law $J_E = \sigma T^4$ where σ is called Stefan's constant. You came across this in

thermodynamics homework where σ was a phenomenological constant. Now we are in the position to attempt to derive it using quantum statistical mechanics.

You probably have seen the ‘use’ of infra-red detectors by MI5/CIA/FSB in series like James Bond/24/Mission Impossible by operatives in the dark. These detectors sense the heat radiated by humans/mammals (which is mostly in the IR and not the visible range of the EM spectrum) and enables the good/bad guys to see the bad/good guys at night.

Real (coloured) objects absorb certain frequencies, emit certain frequencies and reflect others. A **black-body** (and this could be thought of as a definition) absorbs all and emits all frequencies. In thermal equilibrium, absorption and emission by a body must be balanced: this means that good absorbers are also good emitters. Therefore black-bodies are the best absorbers and best emitters of radiation. The absorption/emission balance at equilibrium means that radiation by hot bodies is not an equilibrium phenomenon.

It turns out that a very good model (which fits the experimental data from the last ~ 140 years) for a radiating body is an opaque cavity with a very small hole. In the absence of a hole, there is electromagnetic radiation in the cavity in equilibrium with the walls of the cavity. However we can still understand the system with the hole using equilibrium statistical mechanics as long as the rate of emission is small (the hole is small enough compared to the size of the cavity). For a black-body (the best emitter) the hole can be thought of as completely transparent and the properties of the emitted radiation are exactly the same as the radiation in equilibrium inside the cavity. For a real (coloured) object, the hole will block some of the radiation so that only a fraction (determined by the **emissivity** which is ≤ 1 in general and $= 1$ for black-bodies) of this radiation is emitted by the body ³.

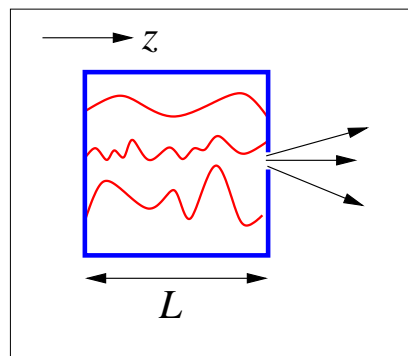


Figure 3: The cavity and emitted blackbody radiation.

Consider a cavity of volume $V = L^3$ with opaque walls maintained at a constant temperature T . Electromagnetic radiation (vacuum fluctuations) is in thermal equilibrium with the walls and we can calculate its properties using equilibrium statistical mechanics. To study the non-equilibrium (and hence emitting/absorbing) situation we can imagine cutting a tiny hole in the walls of the cavity (which is small enough so that it does not affect equilibrium). Then the emitted radiation will have the properties of the equilibrium radiation. This is just a specific example of the fact that in general equilibrium properties can be used to determine behaviour of a system slightly away from equilibrium

³typically of course for a coloured object, the emissivity is frequency dependent but this is often ignored

(called **linear response theory**). The emitted radiation has the same properties as the radiation emitted by a perfectly black body at the same temperature T .

Electromagnetic radiation is due to oscillations of coupled transverse electric and magnetic fields which can be written in terms of a system of harmonic oscillators. Quantizing these fields is an example of the so-called **second quantization** of quantum field theory.

The classical Hamiltonian for the EM field can be written as

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{k}, j} \{ |p_j(\mathbf{k})|^2 + (\omega_j(\mathbf{k}))^2 |x_j(\mathbf{k})|^2 \} \quad (4.2.20)$$

where $j \in \{1, 2\}$ refers to the **2 transverse modes** and \mathbf{k} the wavenumber of the radiation and the frequency of satisfies the dispersion relation, $\omega_j(\mathbf{k}) = c k$ with $k = |\mathbf{k}|$ with $c \simeq 3 \times 10^8 \text{m/s}$ is the speed of light (all EM radiation). For a box of size L , $\mathbf{k} = \frac{2\pi}{L} \mathbf{m}$ where $\mathbf{m} = (m_x, m_y, m_z)$ is a vector of integers. Since $|\mathbf{k}|$ can get arbitrarily large, a classical calculation gives rise to a divergent number of states at high wavenumber (the ultraviolet catastrophe).

The problem can be quantized by turning the Hamiltonian into an operator and quantizing each mode (oscillator) separately.

$$\hat{\mathcal{H}} = \frac{1}{2} \sum_{\mathbf{k}, j} \hbar c k \left(\hat{a}_j^\dagger(\mathbf{k}) \hat{a}_j(\mathbf{k}) + \frac{1}{2} \right) = \frac{1}{2} \sum_{\mathbf{k}, j} \hbar c k \left(\hat{n}_j(\mathbf{k}) + \frac{1}{2} \right) \quad (4.2.21)$$

The eigenstates of each oscillator $|n_j(\mathbf{k})\rangle$ have energies $\mathcal{E}(n_j(\mathbf{k})) = \frac{1}{2} \hbar c k (n_j(\mathbf{k}) + \frac{1}{2})$, $n_j(\mathbf{k}) = 0, 1, 2, 3, \dots$

The energy of the system is then given by summing over all the oscillators :

$$E = \langle \mathcal{H} \rangle = \sum_{\mathbf{k}, j} \hbar c k \left(\frac{1}{2} + \frac{e^{-\beta \hbar c k}}{1 - e^{-\beta \hbar c k}} \right) \quad (4.2.22)$$

We can make the replacement ⁴ : $\sum_{\mathbf{k}} \rightarrow V \int \frac{d^3 k}{(2\pi)^3}$ to get an expression for the energy

$$E = E_0 + \frac{2V}{(2\pi)^3} \int d^3 k \frac{\hbar c k}{e^{\beta \hbar c k} - 1} \quad (4.2.23)$$

where E_0 is the divergent ground-state vacuum energy (which gives rise to the Casimir effect) and the factor **2** comes from the **2 transverse modes**.

Subtracting out the ground-state energy and making the change of variable $\xi = \hbar c k$ we obtain an expression for the energy density

$$\frac{E}{V} = \frac{\hbar c}{\pi^2} \left(\frac{k_B T}{\hbar c} \right)^4 \int_0^\infty \frac{d\xi \xi^3}{e^\xi - 1} \quad (4.2.24)$$

The integral $\int_0^\infty d\xi \xi^3 / (e^\xi - 1) = \pi^4/15$ and so we get

$$\frac{E}{V} = \frac{\pi^2}{15} \hbar c \left(\frac{k_B T}{\hbar c} \right)^4 \quad (4.2.25)$$

⁴ $k_i = 2m_i\pi/L$, m_i integers, $V = L^3$.

If there is a small hole in the cavity with outward normal in the $+z$ -direction then only photons moving in the $+z$ -direction will ‘effuse’ through it. The energy flux radiated is then given by

$$J_E = c_z \frac{E}{V}, \quad (4.2.26)$$

where c_z is the average component of velocity in $+z$ -direction. Recalling the example in the lectures about effusion from a hole in a gas-filled cavity, we can calculate c_z as

$$c_z = c \times \frac{1}{4\pi} \int_0^{\pi/2} 2\pi \sin \theta d\theta \cos \theta = \frac{c}{4}, \quad (4.2.27)$$

with c the speed of light.

This gives rise to the Stefan-Boltzmann law

$$J_E = \sigma T^4 \quad ; \quad \sigma = \frac{\pi^2 k_B^4}{60(\hbar c)^3} = 5.7 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4} \quad (4.2.28)$$

In actual fact this cavity calculation will allow us to calculate not only the total energy flux but also the frequency dependence of the emitted blackbody radiation known as **Planck’s law** for the spectrum of black-body radiation. But we will leave that for now.

4.3 Non-interacting (Ideal) Quantum gases

Now we will apply quantum statistics to the study the statistical mechanics of many particle systems. As we will see the inclusion of quantum mechanics will lead to a number of fundamentally new phenomena which are just not present in classical systems.

Recall that, to remove the Gibbs paradox and make entropy extensive, we had to include the factor of $N!$ when we considered the classical statistical mechanics of ideal gases. This was a result of the intrinsic distinguishability of classical mechanics. Quantum mechanics however removes the need for this.

4.3.1 Hilbert Space of identical particles

For a system of N identical particles, we deal in quantum mechanics (in the position basis) with wave functions (generally called N -particle wave functions) $\langle \{\mathbf{r}_i\} | \Psi \rangle = \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ which (from $|\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$) determine the probabilities of the particles being at positions $\{\mathbf{r}_1, \dots, \mathbf{r}_N\}$:

$$\langle \Psi | \Psi \rangle = 1 \Rightarrow \langle \Psi | \sum_{\{\mathbf{r}_i\}} |\{\mathbf{r}_i\}\rangle \langle \{\mathbf{r}_i\} | \Psi \rangle = \sum_{\{\mathbf{r}_i\}} |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 = 1, \text{ where } \sum_{\{\mathbf{r}_i\}} = \int \prod_{i=1}^N d^3r_i. \quad (4.3.1)$$

Let us consider a particular configuration of particle positions , $\{\mathbf{r}_1, \dots, \mathbf{r}_N\}$, then we exchange the positions of any pair of particles (e.g $\mathbf{r}_1 \rightarrow \mathbf{r}_2, \mathbf{r}_2 \rightarrow \mathbf{r}_1$). The probability of system being in the new configuration must be exactly the same as it was in the initial configuration.

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N)|^2,$$

For a single-valued wavefunction in 3 or more dimension, this implies $\Rightarrow \Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) = \pm \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$.

Particles whose wave functions are odd under exchange of pairs, $\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ are referred to as **fermions** while those which are even under exchange, $\Psi(\mathbf{r}_2, \mathbf{r}_1, \dots, \mathbf{r}_N) = +\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ are called **bosons**.

Fermions and bosons are also identified with quantum-mechanical **spin**: fermions have spin $S_- = 1/2$ integers ($S_- = 1/2, 3/2, 5/2, \dots$) and bosons have $S_+ =$ integers ($S_+ = 1, 2, 3, \dots$) . When rotated by 2π , the phase of the single-particle fermion wavefunction changes by a factor $-1 = e^{i2\pi S_-}$ while the single-particle boson wavefunction phase changes by $+1 = e^{i2\pi S_+}$.

4.3.2 Many-particle quantum states

So one may ask the question exactly how one constructs many particle quantum states. The most useful answer that has been found is : from single particle quantum states.

If we consider a single particle described by a state vector $|\psi\rangle$ in single particle Hilbert space and the $\psi(\mathbf{r}) = \langle \mathbf{r} | \psi \rangle$ is the single particle wave function in a position basis (i.e. expanding the state vector in position states, $|\psi\rangle = \sum_{\mathbf{r}} \psi(\mathbf{r}) |\mathbf{r}\rangle$). The probability that the particle is at position \mathbf{r} is $|\psi(\mathbf{r})|^2$.

We can also use a **momentum** or **plane-wave** basis which are particularly suitable for describing free particles. To do that we define **plane-wave** states $|\mathbf{k}\rangle$ for which applying the momentum operator,

$$\hat{\mathbf{p}} |\mathbf{k}\rangle = \hbar \mathbf{k} |\mathbf{k}\rangle , \quad (4.3.2)$$

where \mathbf{k} is called a **wave-vector** and has dimensions of $[Length]^{-1}$.

Clearly plane wave states are proportional to **momentum** states for which

$$\hat{\mathbf{p}} |\mathbf{p}\rangle = \mathbf{p} |\mathbf{p}\rangle , \quad (4.3.3)$$

the constant of proportionality being \hbar .

We can expand $|\psi\rangle$ in plane wave states,⁵

$$|\psi\rangle = \sum_{\mathbf{k}} \tilde{\psi}(\mathbf{k}) |\mathbf{k}\rangle \quad \text{where} \quad \tilde{\psi}(\mathbf{k}) = \langle \mathbf{k} | \Psi \rangle . \quad (4.3.4)$$

In the absence of any potential, the single particle Hamiltonian operating on plane-wave states is very simple

$$\hat{\mathcal{H}} |\mathbf{k}\rangle = \frac{\hbar^2 |\mathbf{k}|^2}{2m} |\mathbf{k}\rangle = \frac{\hbar^2 k^2}{2m} |\mathbf{k}\rangle \quad (4.3.5)$$

We can construct a quantum description for the many particle system by using the **occupation number** formalism. In this we **count** the number of particles in a particular plane-wave state \mathbf{k} .

⁵It is interesting to note that $\langle \mathbf{r} | \mathbf{k} \rangle = V^{-1/2} e^{i\mathbf{k} \cdot \mathbf{r}}$ and comparing the expansions in position and plane-wave bases, $|\psi\rangle = \sum_{\mathbf{k}} \tilde{\psi}(\mathbf{k}) |\mathbf{k}\rangle$, $|\psi\rangle = \sum_{\mathbf{r}} \psi(\mathbf{r}) |\mathbf{r}\rangle$ we can see that this implies that $\psi(\mathbf{r}) = V^{-1/2} \sum_{\mathbf{k}} \tilde{\psi}(\mathbf{k}) e^{i\mathbf{k} \cdot \mathbf{r}}$, a Fourier series expansion with an inverse $\tilde{\psi}(\mathbf{k}) = V^{-1/2} \sum_{\mathbf{r}} \psi(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}}$.

So if we label the states $\mathbf{k}_0, \mathbf{k}_1, \mathbf{k}_2, \dots$, we can specify the system by the number of particles with wave-vectors (in states), $\mathbf{k}_0, \mathbf{k}_1, \mathbf{k}_2, \dots$:

$$|\{n_{\mathbf{k}}\}\rangle = \frac{1}{\mathcal{N}} |n_0, n_1, n_2, \dots\rangle \quad , \quad (4.3.6)$$

where \mathcal{N} is chosen s.t. $\langle \{n_{\mathbf{k}}\} | \{n_{\mathbf{k}}\} \rangle = 1$.

For **fermions**, antisymmetry under exchange implies (see next section) the Pauli exclusion principle which means that no 2 fermions can occupy the same state. Hence for fermions :

$$n_{\mathbf{k}} = 0 \text{ or } 1 \quad , \quad \forall \mathbf{k} \quad (4.3.7)$$

For **bosons** which are symmetric under exchange, there is no constraint on the particle occupation numbers:

$$n_{\mathbf{k}} = 0, 1, 2, 3, \dots \quad , \quad \forall \mathbf{k} \quad (4.3.8)$$

Hence for non-interacting particles the Hamiltonian acting on occupation number states gives

$$\hat{\mathcal{H}} |\{n_{\mathbf{k}}\}\rangle = \sum_{\mathbf{k}} \mathcal{E}(\mathbf{k}) n_{\mathbf{k}} |\{n_{\mathbf{k}}\}\rangle \quad ; \quad \mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \quad . \quad (4.3.9)$$

Similarly the particle number operator acting on occupation number states gives

$$\hat{n} |\{n_{\mathbf{k}}\}\rangle = \sum_{\mathbf{k}} n_{\mathbf{k}} |\{n_{\mathbf{k}}\}\rangle \quad . \quad (4.3.10)$$

4.3.3 Spin and Statistics

This section is not examinable. However all my find it of interest as it gives the background behind some of the statements in the previous section.

There is a deep topological reason for why in dimensions $d \geq 3$, there are only fermions and bosons. It is due to the fact that the fundamental group (or 1st homotopy group), π_1 is particularly simple for the space of rotations in dimensions $n \geq 3$, $SO(n)$, $\pi_1(SO(3)) = \mathbb{Z}_2$ the cyclic group with 2 elements (since $\pi_1(S^n) = 0$, $n \geq 2 \Rightarrow$ a simple heuristic way to see this is to note that all loops on the surface of the sphere S^n can be contracted to a point). However, this is not true in 2 dimensions since the fundamental group of the space of rotations in two dimensions $SO(2)$ is isomorphic to the group of integers under addition, $\pi_1(SO(2)) = \mathbb{Z}_+ = \{\dots, -2, -1, 0, 1, 2, \dots\}_+$ (this is given by the number of ways a loop can be wrapped around a circle ; $\pi_1(S^1) = \mathbb{Z}_+$). This can be visualized by wrapping a rubber band around one's finger: it can be wrapped once, twice, three times and so on. The wrapping can be in either of two directions, and wrappings in opposite directions will cancel out after a deformation. This has the physical consequence of non-trivial excited states in two-dimensional quantum systems such as the fractional quantum hall effects ⁶.

The link between the statistics of the many-particle wavefunction and quantum mechanical spin of the single particle is called the famous but rather hard to understand **spin-statistics** theorem ⁷.

⁶See for example, F. Wilczek, Phys. Rev. Lett. **49**, 957 (1982)

⁷W. Pauli "The Connection Between Spin and Statistics", Phys. Rev. **58**, 716-722 (1940)

An heuristic argument for the spin statistics theorem - why spin 1/2 particles are fermions, and integer spin particles are bosons is as follows. The “proof” is topological, in that if you rotate a “particle” with strings all over it, the strings are all twisted after 2π radians of rotation, but after 4π the strings can be untangled without moving the object. Similarly, if two “particles” connected by lots of strings are interchanged, the strings are left twisted up exactly as if one particle had been rotated by 2π radians. So the conclusion is that interchanging two particles is topologically indistinguishable from a rotation of one particle by 2π radians - a particle which changes sign after a rotation will be antisymmetric wrt pairwise interchange ⁸.

For a system of N identical particles, there are $N!$ permutations \hat{P} , which form a group S_N . Any permutation can be obtained from a sequence of 2-particle exchanges. The **parity** of a permutation p is defined as

$$(-1)^p = \begin{cases} +1, & \text{if } \hat{P} \text{ involves an } \mathbf{even} \text{ no. of exchanges, } p = 2n \\ -1 & \text{if } \hat{P} \text{ involves an } \mathbf{odd} \text{ no. of exchanges, } p = 2n + 1 \end{cases} .$$

This means that the effective state space has a volume fraction $\frac{1}{N!}$ compared to that of classical phase space.

The action of permutations on an N -particle quantum state leads to a representation of the permutation group in Hilbert space.

Given a general state of particle positions $|\Psi\rangle \equiv |1, 2, \dots, N\rangle$, **bosons** (fully symmetric) are defined by states for which

$$\hat{P}|1, 2, \dots, N\rangle = +|1, 2, \dots, N\rangle ,$$

while **fermions** (fully antisymmetric) are defined by those for which

$$\hat{P}|1, 2, \dots, N\rangle = -|1, 2, \dots, N\rangle ,$$

Clearly the Hamiltonian is symmetric under exchange $\hat{P}\hat{\mathcal{H}} = \hat{\mathcal{H}}$, however there will in general be many e-states of $\hat{\mathcal{H}}$ which have different symmetries under permutations and so we must find a way to restrict our state-space to only those which satisfy the appropriate symmetry. In other words, we will need to take account of the symmetry of the wavefunction in order to be able to construct a suitable of e-states.

Consider N non-interacting particles in a box V for which

$$\hat{\mathcal{H}} = \sum_i \hat{\mathcal{H}}_i = \sum_{i=1}^N -\frac{\hbar^2}{2m} \nabla_i^2 , \quad (4.3.11)$$

each $\hat{\mathcal{H}}_j$ can be diagonalized separately in terms of plane wave states $\{|\mathbf{k}\rangle\}$ with energies $\mathcal{E}(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$ where $k = |\mathbf{k}|$. We can simply make up an N -particle state from products of the single particle plane wave states ⁹: $|\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N\rangle = |\mathbf{k}_1\rangle |\mathbf{k}_2\rangle \cdots |\mathbf{k}_N\rangle$ which satisfies

$$\hat{\mathcal{H}} |\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N\rangle = \sum_{i=1}^N \frac{\hbar^2 k_i^2}{2m} |\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N\rangle$$

However these product states do not have the right symmetry but we can construct **subspaces** of which do have the right symmetry.

⁸Roy R. Gould Am. J. Phys. **63**, 109 (1995)

⁹Projecting on to the coordinate representation $\langle \{\mathbf{r}_i\} | \mathbf{k}_1, \dots, \mathbf{k}_N \rangle = V^{-N/2} \exp\left(\sum_{i=1}^N \mathbf{k}_i \cdot \mathbf{r}_i\right)$

1. The fermionic subspace is made up of asymmetric states constructed by summing all the permutations of a particular plane wave product state with each permutation multiplied by its parity

$$|\{\mathbf{k}_i\}\rangle_- \equiv \frac{1}{\sqrt{N_-}} \sum_P (-1)^P \hat{P} |\mathbf{k}_1, \dots, \mathbf{k}_N\rangle . \quad (4.3.12)$$

If any single-particle label \mathbf{k} appears more than once, it would sum to zero since the sum will also include an equal and opposite contribution obtained by exchanging the 2 labels and multiplying by -1. This subspace can also be written using determinant, called the **Slater** determinant. Hence antisymmetrization is only possible if all the N values of \mathbf{k}_i are different, \Rightarrow equivalent to the **Pauli exclusion principle**. A particular 1-particle state \mathbf{k} appears at most one time, with $n_{\mathbf{k}} = 0, 1$. Therefore there are exactly $N!$ terms in the sum and the requirement $\langle\{\mathbf{k}_i\}|\{\mathbf{k}_i\}\rangle_- = 1$ requires that $N_- = N!$.

2. The bosonic subspace is composed of symmetric states constructed by summing over all the permutations of a particular plane wave product weighting each permutation equally

$$|\{\mathbf{k}_i\}\rangle_+ \equiv \frac{1}{\sqrt{N_+}} \sum_P \hat{P} |\mathbf{k}_1, \dots, \mathbf{k}_N\rangle . \quad (4.3.13)$$

There is no restriction on the allowed values of \mathbf{k}_i . Any particular 1-particle state \mathbf{k} can appear many times, i.e. $n_{\mathbf{k}} = 0, 1, 2, \dots$

Clearly, $\sum_{\mathbf{k}} n_{\mathbf{k}} = N$ and taking the inner product

$$\begin{aligned} 1 = \langle\{\mathbf{k}_i\}|\{\mathbf{k}_i\}\rangle_+ &= \frac{1}{N_+} \sum_{P, P'} \langle\mathbf{k}_1, \dots, \mathbf{k}_N | \hat{P}^\dagger \hat{P}' |\mathbf{k}_1, \dots, \mathbf{k}_N\rangle \\ &= \frac{N!}{N_+} \sum_{P'} \langle\mathbf{k}_1, \dots, \mathbf{k}_N | \hat{P}' |\mathbf{k}_1, \dots, \mathbf{k}_N\rangle \end{aligned} \quad (4.3.14)$$

where we have summed over $N!$ permutations P in the second equality.

$\langle\mathbf{k}_1, \dots, \mathbf{k}_N | \hat{P}' |\mathbf{k}_1, \dots, \mathbf{k}_N\rangle = 0$ unless each of the permuted \mathbf{k} 's are identical and there are $n_{\mathbf{k}}!$ ways of permuting each of the identical \mathbf{k} 's, therefore $N_+ = N! \prod_{\mathbf{k}} n_{\mathbf{k}}!$.

So we can write the general state

$$|\{\mathbf{k}_i\}\rangle = \frac{1}{\sqrt{N_\sigma}} \sum_P \sigma^P \hat{P} |\mathbf{k}_1, \dots, \mathbf{k}_N\rangle , \quad \sigma = \begin{cases} +1, & \text{bosons} \\ -1, & \text{fermions} \end{cases} , \quad N_\sigma = N! \prod_{\mathbf{k}} n_{\mathbf{k}}! .$$

Each fermion or boson state is then uniquely specified by the occupation numbers $\{n_{\mathbf{k}}\}$ of the 1-particle states with the constraint of course that $\sum_{\mathbf{k}} n_{\mathbf{k}} = N$. It is this constraint that makes the quantum statistical mechanics of systems with fixed particle number difficult.

4.4 Grand canonical description

4.4.1 Grand partition function

Calculating partition sums for quantum systems with fixed no. of particles are difficult due to symmetry restrictions on the wave function. They are however much easier in the quantum GCE, where using the **occupation number formalism**, we can calculate the grand partition function

$$\begin{aligned}
 \mathcal{Z}_\sigma &= \text{Tr} \left(e^{-\beta(\hat{\mathcal{H}} - \mu \hat{n})} \right) = \sum_{\{n_{\mathbf{k}}\}} \langle \{n_{\mathbf{k}}\} | e^{-\beta(\hat{\mathcal{H}} - \mu \hat{n})} | \{n_{\mathbf{k}}\} \rangle \\
 &= \sum_{\{n_{\mathbf{k}}\}} \exp \left\{ -\beta \sum_{\mathbf{k}} (\mathcal{E}(\mathbf{k}) - \mu) n_{\mathbf{k}} \right\} = \sum_{\{n_{\mathbf{k}}\}} \left(\prod_{\mathbf{k}} e^{-\beta(\mathcal{E}(\mathbf{k}) - \mu) n_{\mathbf{k}}} \right) \\
 &= \prod_{\mathbf{k}} \sum_{n_{\mathbf{k}}} \left(\prod_{\mathbf{k}} e^{-\beta(\mathcal{E}(\mathbf{k}) - \mu) n_{\mathbf{k}}} \right) = \prod_{\mathbf{k}} \sum_{n_{\mathbf{k}}} e^{-\beta(\mathcal{E}(\mathbf{k}) - \mu) n_{\mathbf{k}}} . \tag{4.4.1}
 \end{aligned}$$

For fermions, $n_{\mathbf{k}} = 0, 1$

$$\mathcal{Z}_- = \prod_{\mathbf{k}} (1 + e^{-\beta(\mathcal{E}(\mathbf{k}) - \mu)}) \tag{4.4.2}$$

For bosons, $n_{\mathbf{k}} = 0, 1, 2, 3, \dots$, (sum to infinity of GP)

$$\mathcal{Z}_+ = \prod_{\mathbf{k}} \left(\frac{1}{1 - e^{-\beta(\mathcal{E}(\mathbf{k}) - \mu)}} \right) \tag{4.4.3}$$

$$\Rightarrow \ln \mathcal{Z}_\sigma = -\sigma \sum_{\mathbf{k}} \ln (1 - z \sigma e^{-\beta \mathcal{E}(\mathbf{k})}) , \quad z = e^{\beta \mu} , \tag{4.4.4}$$

where $\sigma = \begin{cases} +1, & \text{bosons} \\ -1, & \text{fermions} \end{cases}$.

The 1-particle states are occupied independently so the *normalised* probability of finding the system in state $\{n_{\mathbf{k}}\}$ is

$$p_\sigma(\{n_{\mathbf{k}}\}) = \frac{1}{\mathcal{Z}_\sigma} \prod_{\mathbf{k}} e^{-\beta(\mathcal{E}(\mathbf{k}) - \mu) n_{\mathbf{k}}} \tag{4.4.5}$$

so the mean occupation number of state \mathbf{k} is

$$\langle n_{\mathbf{k}} \rangle_\sigma = \sum_{\{n_{\mathbf{k}}\}} n_{\mathbf{k}} p_\sigma(\{n_{\mathbf{k}}\}) = \prod_{\mathbf{k}} \sum_{n_{\mathbf{k}}} (n_{\mathbf{k}} p_\sigma(\{n_{\mathbf{k}}\})) \tag{4.4.6}$$

$$\Rightarrow \langle n_{\mathbf{k}} \rangle_\sigma = -\frac{\partial \ln \mathcal{Z}_\sigma}{\partial (\beta \mathcal{E}(\mathbf{k}))} = \frac{1}{z^{-1} e^{\beta \mathcal{E}(\mathbf{k})} - \sigma} \tag{4.4.7}$$

$$\sigma = +1, \quad \langle n_{\mathbf{k}} \rangle_+ = \frac{1}{z^{-1} e^{\beta \mathcal{E}(\mathbf{k})} - 1}, \quad \text{Bose-Einstein statistics} \tag{4.4.8}$$

$$\sigma = -1, \quad \langle n_{\mathbf{k}} \rangle_- = \frac{1}{z^{-1} e^{\beta \mathcal{E}(\mathbf{k})} + 1}, \quad \text{Fermi-Dirac statistics} \tag{4.4.9}$$

From this we can obtain the average particle number

$$N_\sigma = \sum_{\mathbf{k}} \langle n_{\mathbf{k}} \rangle_\sigma = \sum_{\mathbf{k}} \frac{1}{z^{-1} e^{\beta \mathcal{E}(\mathbf{k})} - \sigma}, \quad (4.4.10)$$

and similarly the average energy

$$E_\sigma = \sum_{\mathbf{k}} \mathcal{E}(\mathbf{k}) \langle n_{\mathbf{k}} \rangle_\sigma = \sum_{\mathbf{k}} \frac{\mathcal{E}(\mathbf{k})}{z^{-1} e^{\beta \mathcal{E}(\mathbf{k})} - \sigma}, \quad (4.4.11)$$

Quantum particles of spin S have $2S + 1$ spin states characterised by spin quantum number $m_S = -S, -S + 1, \dots, S - 1, S$. In the absence of magnetic fields all the spin states have the same energy giving rise to a spin degeneracy factor $\gamma = 2S + 1$ which we must multiply all our averages by.