We are now going to consider the statistical mechanics of quantum systems. In particular we shall study the macroscopic properties of a collection of many \((N \sim 10^{23})\) identical and indistinguishable Fermions and Bosons with overlapping wavefunctions. We will study a number of systems whose macroscopic thermodynamic behavior is dominated by quantum mechanics, including:

1) Electrons in a solid, and superconductivity
2) Liquid \(^4\)He and superfluidity
3) Photons in a box (black body radiation)
4) Ultra-cold atoms in an optical lattice (Bose-Einstein condensation)

The systems we will consider will be at a finite temperature \(T\). Temperature is a measure of the average kinetic energy of the particles in the system. Many of the particles will occupy quantum energy states above the ground state. Because the number of particles \(N\) is so large, there are many microscopic configurations of the particles that are consistent with a fixed particle number (\(N\)) and total energy (\(E\)). The fundamental assumption of statistical mechanics is that the system explores all the possible microscopic states that have the same energy, with equal likelihood. This is the concept of ‘ergodicity’ embodied in the **ergodic hypothesis** of statistical mechanics.

Consider the example of 3 particles weakly interacting in a one-dimensional infinite square well. The particles have single-particle eigenenergies of \(E_q = \frac{q^2 \pi^2 h^2}{2ma^2}\).

If the total energy of the three particles is \(E = E_A + E_B + E_C = (q_A^2 + q_B^2 + q_C^2) \frac{\pi^2 h^2}{2ma^2} = 243 \frac{\pi^2 h^2}{2ma^2}\), what are the possible microscopic configurations consistent with this total energy? The answer depends on what kind of particles we are talking about. For the case of completely distinguishable Newtonian particles, we live under the fiction that each particle has a unique label, and there are 10 possible states:

Distinguishable: \((9,9,9); (3,3,15); (3,15,3); (15,3,3); (5,7,13); (5,13,7); (7,5,13); (7,13,5); (13,5,7); (13,7,5)\), where the triplet represents the quantum numbers \((q_A, q_B, q_C)\).

For the case of indistinguishable Fermions, we cannot have multiple occupation of the same quantum state. In addition we cannot distinguish the particles once their wavefunctions overlap, so in fact there is only one state possible – that in which the particles occupy 3 distinct states: 5, 7 and 13 (without specifying which particle is in which state!) We need a better / new notation to describe this situation. We should simply specify the occupation numbers of each state as follows: \(n_5 = 1, n_7 = 1, n_{13} = 1, n_i = 0\) for all \(i\) not equal to 5, 7 or 13.

The case of indistinguishable Bosons is similar, except that we do not have to satisfy the Pauli exclusion principle. In this case there are three distinct quantum states of the 3 indistinguishable particles:

Configuration 1: \(n_9 = 3, n_i = 0\) for all \(i\) not equal to 9.
Configuration 2: \(n_3 = 2, n_{15} = 1, n_i = 0\) for all \(i\) not equal to 3 and 15.
Configuration 3: \(n_5 = 1, n_7 = 1, n_{13} = 1, n_i = 0\) for all \(i\) not equal to 5, 7 or 13.
To generalize this process to a large number of particles $N$, consider the following exercise. Consider a general system that has an infinite number of discrete bound states, with energies labeled as $E_i$, where $i$ runs from 1 to infinity. Each state has degeneracy $g_i$. [Recall that in the unperturbed hydrogen atom with no spin the list of quantum numbers is $n, \ell, m$, and the degeneracy of the states is equal to $n^2$. This means for example that for $n = 100$ there are $g_{100} = 10^4$ distinct lists of quantum numbers $n, \ell, m$ all with the same energy: $-13.6 \text{ eV } \frac{1}{100^2}$! The message is that degeneracy in quantum systems generally grows very quickly with increasing eigen-energy.] We have the job of distributing the $N$ particles into these states, subject to two constraints: the total number of particles is fixed at $N \left( \sum_{i=1}^{\infty} n_i = N \right)$, and the total energy is fixed at $E \left( \sum_{i=1}^{\infty} n_i E_i = E \right)$.

How can we possibly do this? The approach is to calculate all of the possible microscopic configurations of the particles distributed into the available states (at fixed $N$ and $E$) and then find the configuration that is most likely to occur, assuming ergodicity. Essentially we must calculate the relative probability of finding every possible microscopic configuration, and seek to maximize that probability. This state, and many others that differ from it only slightly, will dominate the thermodynamic properties of the system.

First we will calculate the number of ways that $n_s$ particles can be distributed into state $s$ of energy $E_s$ and degeneracy $g_s$. This will be called $P_s$. Next we will calculate the total number of arrangements for an entire set of occupation numbers $n_1, n_2, n_3, n_4, \ldots n_s, \ldots$ This will be the statistical weight $W$ of the arrangement $(n_1, n_2, n_3, n_4, \ldots n_s, \ldots)$:

$$W(n_1, n_2, \ldots, n_s, \ldots) = \prod_{s=1}^{\infty} P_s = P_1 P_2 P_3 P_4 \ldots P_s \ldots$$

This weight will be proportional to the probability of finding this particular distribution of occupation numbers. {Note that if $n_s = 0$, there is only one way to make that happen, so the corresponding $P_s = 1$.}

The next step is to maximize $W$ by varying all of the occupation number values subject to the number and total energy constraints. We will then do thermodynamics with the most probable microscopic configuration.

Consider 3 cases:
1) Distinguishable classical particles
2) Indistinguishable identical Fermions
3) Indistinguishable identical Bosons

**Distinguishable classical particles:** This is something of a fiction in the sense that each particle has a unique identity and we can keep track of its location and energy with arbitrary precision. Start with the ground state ($i = 1$, energy $E_1$ with degeneracy $g_1$). How many ways are there to put $n_1$ distinguishable particles in this energy level? The answer is;
\[ P_1 = \binom{N}{n_1} g_1^{n_1} , \] where the binomial coefficient is \[ \binom{N}{n_1} = \frac{N!}{n_1!(N-n_1)!} . \] The binomial coefficient arises because we can distinguish each particle and there are many distinct ways to choose a subset \( n \) of all the particles \( N \), without regard to the order in which they are chosen. The particles can each be put into any of \( g_1 \) possible states, hence the factor of \( g_1^{n_1} \).

When constructing \( P_2 \) there is a similar factor, except that there are now only \( N-n_1 \) particles to start with. Hence \[ P_2 = \binom{N-n_1}{n_2} g_2^{n_2} , \] and so on. When we construct the relative statistical weight \( W \), the result has a lot of cancellation:

\[
W = \frac{N!g_1^{n_1}}{n_1!(N-n_1)!} \cdot \frac{(N-n_1)!g_2^{n_2}}{n_2!(N-n_2)!} \cdot \frac{(N-n_1-n_2)!g_3^{n_3}}{n_3!(N-n_1-n_2-n_3)!} \cdots
\]

\[ W_{Dist} (n_1, n_2, ..., n_s, ...) = N! \prod_{s=1}^{\infty} \frac{g_s^{n_s}}{n_s!} . \] The big Pi is a product.

**Indistinguishable identical Fermions:** In this case we do not have the problem of choosing \( n \) particles out of \( N \) since they are all completely identical and there is no need to enumerate how such choices can be made – there is only one way. Instead we are now concerned with enforcing the Pauli exclusion principle. In this case it means that \( n \) must be less than or equal to \( g_s \), but never greater. If \( n_s \) is less than \( g_s \) we have the freedom to distribute the particles many different ways. In fact there are \( \binom{g_s}{n_s} \) ways to put the \( n_s \) particles into the \( g_s \) available states. Note that if \( n_s = g_s \), this reduces to a factor of 1 since there is only one way to distribute one of the identical particles to each available quantum state. Similarly if \( n_s = 0 \) there is only one way to accomplish that, so \( P_s = 1 \). Finally, if \( n_s > g_s \) there would be a violation of the Pauli exclusion principle. This creates the factorial of a negative number in the denominator from \( (g_s - n_s)! \). From the properties of the Gamma function, which is the generalization of the factorial function to the complex plane, we know that the factorial of negative integers evaluates to infinity, hence the corresponding \( P_s \) is zero, and the corresponding statistical weight \( W \) is also zero. This is a strict enforcement of the Pauli exclusion principle! Now the statistical weight is:

\[
W_{Fermions} (n_1, n_2, ..., n_s, ...) = \prod_{s=1}^{\infty} \frac{g_s!}{n_s! (g_s - n_s)!}
\]

**Indistinguishable identical Bosons:** From the treatment in Griffiths, one finds the result for the statistical weight is:

\[
W_{Bosons} (n_1, n_2, ..., n_s, ...) = \prod_{s=1}^{\infty} \frac{(n_s + g_s - 1)!}{n_s! (g_s - 1)!}
\]
The next step is to maximize \( W(n_1, n_2, \ldots, n_s, \ldots) \) by varying all of the occupation numbers, subject to the number and total energy constraints: \( \sum_{i=1}^{N} n_i = N \) and \( \sum_{i=1}^{N} n_i E_i = E \).

We will include the constraints using the method of Lagrange multipliers. This method allows one to perform a constrained maximization. We will form a new function to maximize, namely;

\[ G(n_1, n_2, \ldots, n_s, \alpha, \beta) = W(n_1, n_2, \ldots, n_s, \ldots) + \alpha \left( N - \sum_{i=1}^{\infty} n_i \right) + \beta \left( E - \sum_{i=1}^{\infty} n_i E_i \right) \]

The last two terms are adding zero, dressed by the Lagrange multipliers. These two terms will modify the gradient of the function in the high-dimensional space spanned by the \( n_s \) values. To maximize this function we must enforce these conditions:

\[ \frac{\partial G}{\partial n_s} = 0 \quad \forall s \quad \text{and} \quad \frac{\partial G}{\partial \alpha} = \frac{\partial G}{\partial \beta} = 0 . \]

The form of \( G \) already satisfies the last two conditions.

We found the statistical weight \( W \) of the arrangement \((n_1, n_2, n_3, n_4, \ldots, n_s, \ldots)\):

\[ W(n_1, n_2, \ldots, n_s, \ldots) = \prod_{s=1}^{\infty} P_s , \]

for three different types of statistics. This weight is proportional to the probability of finding this particular distribution of occupation numbers.

1) Distinguishable classical particles \( W_{\text{Dist}}(n_1, n_2, \ldots, n_s, \ldots) = N! \prod_{s=1}^{\infty} \frac{g_s^{n_s}}{n_s!} \) (1)

2) Indistinguishable identical Fermions \( W_{\text{Fermions}}(n_1, n_2, \ldots, n_s, \ldots) = \prod_{s=1}^{\infty} \frac{g_s!}{n_s!(g_s - n_s)!} \) (2)

3) Indistinguishable identical Bosons \( W_{\text{Bosons}}(n_1, n_2, \ldots, n_s, \ldots) = \prod_{s=1}^{\infty} \frac{(n_s + g_s - 1)!}{n_s!(g_s - 1)!} \) (3)

Because of the products appearing in Eqs. (1)-(3), it is easier to maximize the logarithm of \( W \), rather than \( W \) itself. This will yield the same result since \( W \) and \( \ln W \) have maxima at the same values of their arguments. Taking the natural log of a product is equivalent to the sum of the natural logs (e.g. \( \ln(xy) = \ln(x) + \ln(y) \)), hence \( \ln(\prod_{s=1}^{\infty} n_s) = \sum_{s=1}^{\infty} \ln(n_s) \). The newly defined \( G \) for distinguishable particles now is:

\[ G_{\text{Dist}}(n_1, n_2, \ldots, n_s, \ldots, \alpha, \beta) = \ln(N! \prod_{s=1}^{\infty} \frac{g_s^{n_s}}{n_s!}) + \alpha \left( N - \sum_{i=1}^{\infty} n_i \right) + \beta \left( E - \sum_{i=1}^{\infty} n_i E_i \right) \]

\[ = \ln N! + \sum_{s=1}^{\infty} (n_s \ln g_s - \ln n_s!) + \alpha \left( N - \sum_{i=1}^{\infty} n_i \right) + \beta \left( E - \sum_{i=1}^{\infty} n_i E_i \right) \]
To take the derivative of $G$ with respect to a particular $n_s$, we must now decide what to do with the logarithm of $n_s!$. One approach is to employ Stirling’s approximation: $\ln x! \cong x \ln x - x$, good for $x \gg 1$ (it also works for $x = 0$). With this approximation, $G_{\text{Dist}}$ becomes:

$$G_{\text{Dist}}(n_1, n_2, \ldots, n_s, \ldots, \alpha, \beta) \cong \ln N! + \sum_{s=1}^{N} (n_s \ln g_s - n_s \ln n_s + n_s) + \alpha \left( N - \sum_{i=1}^{N} n_i \right) + \beta \left( E - \sum_{i=1}^{N} n_i E_i \right)$$

Taking the derivative of $G$ with respect to some particular $n_s$ (called $n_i$ in the lecture) and setting it equal to zero (to find the maximum), yields:

$$n_s = g_s e^{-(\alpha + \beta E_i)}$$

Distinguishable particles

For the other cases one gets

$$n_s = \frac{g_s}{e^{-(\alpha + \beta E_i)} + 1}$$

Identical Fermions

$$n_s = \frac{g_s}{e^{-(\alpha + \beta E_i)} - 1}$$

Identical Bosons

What are the Lagrange multipliers $\alpha$ and $\beta$? They are determined by the number and energy constraints $\sum_{i=1}^{N} n_i = N$ and $\sum_{i=1}^{N} n_i E_i = E$. The challenge is to determine the energies and degeneracies of all of the single-particle states of the system - this is the hardest part of quantum statistical mechanics. Calculating the total energy of an ideal gas, which is a relatively easy case, Griffiths (pp. 239-240) finds that $\beta = 1/ k_B T$, where $T$ is the absolute temperature of the gas. The other parameter $\alpha$ is re-defined in terms of the chemical potential $\mu$ as $\alpha \equiv -\mu \beta$. The chemical potential is a measure of how much energy is required to change the particle number of the system from $N$ to $N + 1$. The three distribution functions can now be written as:

$$n_s = g_s e^{-(E_s - \mu)/k_B T}$$

Distinguishable particles

$$n_s = \frac{g_s}{e^{+(E_s - \mu)/k_B T} + 1}$$

Identical Fermions

$$n_s = \frac{g_s}{e^{+(E_s - \mu)/k_B T} - 1}$$

Identical Bosons

We can now do statistical mechanics.