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Lecture 10: Quantum Statistical Mechanics

1 Introduction

So far, we have been considering mostly classical statistical mechanics. In classical mechanics, energies are continuous, for example momenta $\vec{p}$ and hence kinetic energy $E=\frac{\vec{p}^2}{2m}$ can be any real number. Positions $\vec{q}$ can also take any continuous values in a volume $V=L^3$. Thus the number of states Ω, the entropy S, the partition function Z, all involve $\int dq dp$ which is formally infinite. We regulated these infinities by artificially putting limits Δq and Δp on the positions and momenta that are allowed, and we found that physical predictions we made did not depend on Δp and Δq. Quantum statistical mechanics will allow us to remove these arbitrary cutoffs.

In quantum mechanics there are two important changes we must take into account. First, position, momentum and energy are in general quantized. We cannot specify the position and momentum independently, since they are constrained by the uncertainty principle $\Delta p \Delta q \leqslant \frac{\hbar}{2}$. For example, the momenta modes of a particle in a box of size L are quantized as $p_n = \frac{2\pi}{L}\hbar n$, with n an integer. There is no extra degree of freedom associated with position. When summing over states, we sum over $n=\frac{L p_n}{2\pi\hbar}$ only, not over q. However, in the continuum limit we can replace the sum over n with an integral, and suggestively write $L=\int dq$. That is, the quantum sum gets replaced by an integral as

$$\sum_n \rightarrow \int dn = \frac{L}{2\pi\hbar}\int dp = \int \frac{dq dp}{h} \tag{1}$$

Recall that in classical statistical mechanics when we first computed Ω in the microcanonical ensemble, we had to arbitrarily break up position and momentum into sizes Δq and Δp. Eq. (1) justifies the replacement $\Delta p \Delta q \rightarrow h$ that we previously inserted without proof in the Sackur-Tetrode equation and elsewhere.[1] Note that the integral measure has a factor of h not $\hbar$. We'll do conversions between sums and integrals like in Eq. (1) in more detail in deriving the density of states over the next several lectures.

Quantization is important when we are *not* in the continuum limit. One regime where quantum effects are clearly important is when the temperature is of order the lowest energy of the system, $k_B T \sim \varepsilon_0$. For example, classically, each vibrational mode of a molecule contributes $N k_B$ to the heat capacity, but at low temperature, the measured heat capacity does not show this contribution. In quantum statistical mechanics, the vibrational contribution to the heat capacity is cut off at temperatures below $k_B T \lesssim \hbar\omega_0$, with ω_0 the vibrational frequency, in agreement with measurements. We discussed this effect in Lecture 7.

The second quantum effect we need to account for has to do with identical particles. In quantum mechanics, identical particles of half-integer spin, like the electron, can never occupy the same state, by the Pauli exclusion principle. These particles obey **Fermi-Dirac statistics**. Identical particles of integer spin, like the photon, can occupy the same state but the overall wavefunction must be symmetric in the interchange of the two particles. Integer-spin particles obey **Bose-Einstein statistics.**

We discussed indistinguishability before in Lecture 6, in the context of the second law of thermodynamics and the Gibbs paradox. In that lecture, we found that we could decide if we want to treat particles as distinguishable or indistinguishable. If we want to treat the particles as distinguishable, then we must include the entropy increase from measuring the identity of all the particles to avoid a conflict with the second law of thermodynamics. Alternatively, if

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[1] Eq. (1) makes the appearance of dq seem like a trick. This is an artifact of using momentum eigenstates for our basis. If we used something symmetric in p and q like coherent states, the product $dpdq$ would appear more naturally.

we never plan on actually distinguishing them, we can treat them as indistinguishable. We do this by adding a factor of $\frac{1}{N!}$ to the number of states Ω, i.e. instead of $\Omega \sim V^N$ we take $\Omega \sim \frac{1}{N!}V^N$; then there is automatically no conflict with the second law of thermodynamics. This kind of classical indistinguishable-particle statistics, with the $N!$ included, is known as **Maxwell-Boltzmann statistics.** Quantum identical particles is a stronger requirement, since it means the multiparticle wavefunction must be totally symmetric or totally antisymmetric. In a classical system, the states are continuous, so there is exactly zero chance of two particles being in the same state. Thus, the difference among Fermi-Dirac, Bose-Einstein and Maxwell-Boltzmann statistics arises entirely from situations were a single state has a nonzero change of being multiply occupied.

2 Bosons and fermions

The wavefunction $\psi(x,s)$ of an electron depends on the coordinate x and the spin $s=\pm\frac{1}{2}$. When there are two electrons, the wavefunction depends on two coordinates and two spins. We can write it as $\psi(x_1,s_1,x_2,s_2)$. Thus $|\psi(x_1,s_1,x_2,s_2)|^2$ gives the probability of finding one electron at x_1 with spin s_1 *and* one electron at x_2 with spin s_2. Every electron is identical and therefore[2]

$$|\psi(x_1,s_1,x_2,s_2)|^2 = |\psi(x_2,s_2,x_1,s_1)|^2 \tag{2}$$

If the modulus of two complex numbers is the same, they can only differ by a phase. We thus have

$$\psi(x_1,s_1,x_2,s_2) = \eta\psi(x_2,s_2,x_1,s_1) \tag{3}$$

for some phase $\eta = e^{i\theta}$ with $|\eta| = 1$. If we swap the particles back, we then find

$$\psi(x_1,s_1,x_2,s_2) = \eta\psi(x_2,s_2,x_1,s_1) = \eta^2\psi(x_1,s_1,x_2,s_2) \tag{4}$$

So that $\eta^2 = 1$ and $\eta = \pm 1$. We call particles with $\eta = 1$ **bosons** and those with $\eta = -1$ **fermions**.

Particles come with different spins $s = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots$. A beautiful result from quantum field theory is that particles with integer spins, $s = 0, 1, 2, \cdots$ are bosons and particles with half-integrer spins $s = \frac{1}{2}, \frac{3}{2}, \cdots$ are fermions. This correspondance is known as the **spin-statistics theorem**.

As an aside, I'll give a quick explanation of where the spin-statistics theorem comes from. First we need to know what spin means. The spin determines how the state $|\psi\rangle$ changes under rotations. For example, say a particle is localized at $x=0$, so $\psi(\vec{x}) = \langle x|\psi\rangle = \delta^3(x)$, and has spin pointing in the z direction, so $j_z = s$. Now rotate it around the x axis by an angle θ. Doing so means it will pick up a phase determined by the spin

$$|\psi\rangle \rightarrow e^{is\theta}|\psi\rangle \tag{5}$$

In other words, the spin s is the coefficient of θ in the phase. For example, write the electric field vector $\vec{E}$ as a complex number $z = E_x + iE_y$. Then under a rotation by angle θ, $z \rightarrow e^{i\theta}z$, so $s=1$ according to Eq. (5). This tells us that photons (the quanta of the electric field) have spin 1. Under a 360° rotation ($\theta = 2\pi$), we are back to where we started. But that doesn't mean that $|\psi\rangle \rightarrow |\psi\rangle$. Indeed, we see directly that if s is a half-integer, then $|\psi\rangle = -|\psi\rangle$ while if s is an integer then $|\psi\rangle \rightarrow |\psi\rangle$. Now consider a two particle state, $\psi(x_1,\uparrow,x_2,\uparrow)$ with $s=\uparrow$ denoting spin up in the z direction. Now we rotate by 180° around the center between x_1 and x_2, this interchanges the particles, but adds a phase $e^{is\pi}$ for particle 1 and another phase $e^{is\pi}$ for particle 2. So the interchange adds a factor of $e^{2\pi is} = \pm 1$ total to the wavefunction. This is exactly the factor η in Eq. (3). Thus $\eta = e^{2\pi is}$ which is 1 for integer spins and -1 for half-integer spins. In other words, integer spin particles are bosons and half-integer spin particles are fermions.

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[2] Electrons are identical by definition, since if every electron were not identical, we could give the different "electrons" different names. For example, there's a particle called the muon which is similar to the electron but heavier. Thus the electron/muon wavefunction will have $\psi(x_1,x_2) \neq \psi(x_2,x_1)$. Unless there are an infinite number of possible quantum numbers that we can use to tell all electrons apart, some of them will be identical and satisfy $|\psi(x_1,s_1,x_2,x_2)|^2 = |\psi(x_2,s_2,x_1,s_1)|^2$. The identical particles for which quantum statistics applies are, by definition, these identical ones.

The main implication of the spin-statistics theorem for statistical mechanics is the Pauli exclusion principle: no two fermions (like electrons) with the same quantum numbers (like spin) can occupy the same state. To see this, say the wavefunction for an state is $\psi_0(x,\, s)$. Then if two particles were in the same state with the same spin then $\psi(x_2, s_2, x_1, s_1) = \psi_0(x_1, s_1)\psi_0(x_2, s_2)$. This is symmetric under interchange. So if $\psi(x_2, s_2, x_1, s_1) = -\psi(x_1, s_1, x_2, s_2)$, as for fermions, then ψ must vanish. Instead, for fermions we can only have $\psi(x_2, s_2, x_1, s_1) = \psi_0(x_1, s_1)\psi_1(x_2, s_2)$ with two *different* single particle wavefunctions ψ_0 and ψ_1. More generally, each identical fermion must be in a different state, so when we pile N fermions into a system, they start filling the energy levels from the bottom up.

2.1 Three types of statistics

There are 3 types of statistics we will discuss

- In (classical) Maxwell-Boltzmann statistics any particle can be in any state and an overall factor of $\frac{1}{N!}$ for indistinguishability is added *ad hoc* to the number of states $\Omega = \frac{1}{N!}\sum_k 1$ (microcanonical ensemble) or to partition function: $Z = \frac{1}{N!}\sum_k e^{-\beta E_k}$ (canonical ensemble).
- In Bose-Einstein statistics multiple particles can occupy each single-particle state. But when they do, there is only one combined state with the multiple particles in it. No $N!$ is added: $Z = \sum e^{-\beta E_k}$.
- In Fermi-Dirac statistics, no two particles can occupy the same state. No $N!$ is added and $Z = \sum e^{-\beta E_k}$.

Let's compare the situations with an example. Suppose there are 2 particles and 3 possible single-particle states with energies ε_1, ε_2 and ε_3. These energies do not have to be different, but let's suppose they are for simplicity (the single-particle states could have the same energies but different quantum numbers, such as different spin or position or vibrational excitation along a different axis). For Maxwell-Boltzmann statistics, the particles are treated as distinguishable for counting states, and the $\frac{1}{N!}$ is added at the end. Denoting the two particles A and B, the possible states and canonical partition function (with $\beta = 1$ for simplicity) in this case is:

ε_1	ε_2	ε_3
AB		
A	B	
A		B
B	A	
	AB	
	A	B
B		A
	B	A
		AB

,

$$Z_{\text{MB}} = \frac{1}{2!}[e^{-2\varepsilon_1} + e^{-2\varepsilon_2} + e^{-2\varepsilon_3} + 2e^{-\varepsilon_1-\varepsilon_2} + 2e^{-\varepsilon_1-\varepsilon_3} + 2e^{-\varepsilon_2-\varepsilon_3}] \tag{6}$$

The $\frac{1}{2!}$ is the identical particles factor. Note that we treat the two particles as different when constructing the partition function, then divide by $N!$.

For Bose-Einstein statistics, the possible states and canonical partition function are

ε_1	ε_2	ε_3
AA		
A	A	
A		A
	AA	
	A	A
		AA

,

$$Z_{\text{BE}} = e^{-2\varepsilon_1} + e^{-2\varepsilon_2} + e^{-2\varepsilon_3} + e^{-\varepsilon_1-\varepsilon_2} + e^{-\varepsilon_1-\varepsilon_3} + e^{-\varepsilon_2-\varepsilon_3} \tag{7}$$

Note that we treat the particles as identical, so $AA = BA = AB$ is one state. No $N!$ is added.

For Fermi-Dirac statistics, the possible states and canonical partition function are

ε_1	ε_2	ε_3
A	A	
A		A
	A	A

$$, \qquad Z_{\text{FD}} = e^{-\varepsilon_1-\varepsilon_2} + e^{-\varepsilon_1-\varepsilon_3} + e^{-\varepsilon_2-\varepsilon_3} \tag{8}$$

Note that there are 9 two-particle states for the Maxwell-Boltzmann case, 6 for the boson case and only 3 for the fermion case. The 3 two-particle states in the fermion case are the ones where each particle has a different energy. If there were m possible energy levels instead of 3 for the two particles, then there would be

$$n_{\text{fermi}} = \begin{pmatrix} m \\ 2 \end{pmatrix} = \frac{1}{2}m^2 - \frac{1}{2}m \tag{9}$$

possible two-fermion states. The number of boson two-particle states would include all the possible fermion ones plus the m states where both particles have the same energy, so

$$n_{\text{bose}} = n_{\text{fermi}} + m = \frac{1}{2}m^2 + \frac{1}{2}m \tag{10}$$

The number of classical two-particle states is $n_{\text{class}} = m^2$. To compare to the fermion or boson cases, note that in the limit that $k_B T \gg \varepsilon_i$ for all the energies, the Boltzmann factors all go to 1 so the partition function Z just counts the number states. Thus the effective number of states in Maxwell-Boltzmann statistics is

$$n_{\text{MB}} = Z_{\text{MB}}(k_B T \gg \varepsilon_j) = \frac{1}{2!} n_{\text{class}} = \frac{1}{2}m^2 \tag{11}$$

Thus we see that for 2 particles when the number of thermally accessible energies m is large, the number of two-particle states is the same in all three cases.

For N particles and m energy levels, the same analysis applies. The difference between the fermion and boson cases is due to the importance of states where more than one particle occupy the same energy level. The number of such states is always down by at least a factor of m from the number of states where all the particles have different energies. Thus when m gets very large, so that there are a large number of thermally accessible energy levels, then the distinction between bosons and fermions starts to vanish. In other words, $m \gg N$ almost all the microstates will have all the particles at different energies. For any particular set of N energies for the N particles there would be $N!$ classical assignments of the particles to the energy levels, but only one quantum assignment. This explains why the $\frac{1}{N!}$ Gibbs factor for identical particles in Maxwell-Boltzmann statistics is consistent with quantum statistical mechanics. We will make more quantitative the limit in which quantum statistics is important in Section 4.

3 Non-interacting gases

Next we compute the probability distributions for the different statistics, assuming only that the particles are non-interacting. We call the non-interacting systems *gases*, i.e. Bose gas and Fermi gas. Neglecting interactions allows us to write the total energy as the sum of the individual particle energies. For photons, neglecting interactions is an excellent approximation since Maxwell's equations are linear – the electromagnetic fields does not interact with itself. For fermions, like electrons, even though there are electromagnetic interactions, because fermions like to stay away from each other (due to the Pauli exclusion principle), the interactions are generally weak. Thus the non-interacting-gas approximation will be excellent for many bosonic and fermionic systems, as we will see over the next 5 lectures.

Let us index the possible energy levels each particle can have by $i=1,2,3,\cdots$. The energy of level i is ε_i. For example, a particle in a box of size L has quantized momenta, $p_n=\frac{n\pi}{L}\hbar$ and energies $\varepsilon_n=\frac{p_n^2}{2m}$. In any microstate with a given N and E there will be some number n_i of particles at level i, so $\sum n_i=N$ and $\sum n_i\varepsilon_i=E$. It is actually very difficult to work with either the microcanonical ensemble (fixed N and E) or the canonical ensemble (fixed N and T) for quantum statistics. For example, with 2 particles, the canonical partition function for a Bose gas would be

$$Z_{\mathrm{BE}}=\sum_{i=1}^{\infty}\sum_{j=i}^{\infty}e^{-\beta(\varepsilon_i+\varepsilon_j)} \tag{12}$$

You can check that with only 3 energy levels, this reproduces Eq. (7). Note that we must have $j\geqslant i$ in the second sum to avoid double counting the (i,j) and (j,i) states. For N particles, we would need N indices and can write

$$Z_{\mathrm{BE}}=\sum_{i_1\leqslant i_2\leqslant\cdots\leqslant i_N}e^{-\beta(\varepsilon_{i_1}+\varepsilon_{i_2}+\cdots+\varepsilon_{i_N})} \tag{13}$$

Doing the sum this way over N indices is very difficult; even in the simplest cases it is impossible to do in closed form. For Fermi-Dirac statistics the partition function can be written the same way with the sum over indices with strict ordering: $i_1<i_2<\cdots<i_N$. It is also very hard to do.

Conveniently, the grand canonical ensemble comes to the rescue. In the grand canonical ensemble, we sum over N and E, fixing instead μ and T. The grand partition function is

$$\mathcal{Z}=\sum_{N,E}e^{-\beta(E-N\mu)} \tag{14}$$

Since $\sum n_i=N$ and $\sum n_i\varepsilon_i=E$ the grand partition function can also be written as

$$\mathcal{Z}=\prod_{\text{single particle states } i}\ \sum_{n_i=0}^{\infty}e^{-n_i\beta(\varepsilon_i-\mu)} \tag{15}$$

where n_i is the number of particles in state i. To see that this agrees with Eq. (14) consider that each term in the product over i picks one factor from each term in the sum over n_i. Since all possible values of ε_i and n_i are included once, we reproduce the sum over all possible N and E with $\sum n_i=N$ and $\sum n_i\varepsilon_i=E$. For example, if $n_i=0,1,2,\cdots$ are allowed (as in a Bose system), then Eq. (15) means (with $\beta=\mu=1$ for simplicity):

$$\mathcal{Z}=1+e^{\mu-\varepsilon_1}+e^{2\mu-2\varepsilon_1}+\cdots+e^{2\mu-2\varepsilon_2}+e^{2\mu-\varepsilon_1-\varepsilon_2}+\cdots+e^{\mu-\varepsilon_3}+\cdots+e^{9\mu-6\varepsilon_1-2\varepsilon_2-\varepsilon_3}+\cdots \tag{16}$$

$$=(1+e^{\mu-\varepsilon_1}+e^{2\mu-2\varepsilon_1}+\cdots)(1+e^{\mu-\varepsilon_2}+e^{2\mu-2\varepsilon_2}+\cdots)(1+e^{\mu-\varepsilon_3}+e^{2\mu-2\varepsilon_3}+\cdots)\cdots \tag{17}$$

The second line shows all terms with $N=2$ and energies ε_1, ε_2, ε_3 and agrees with the explicit enumeration in Eq. (7). The equivalence of Eq. (15) and Eq. (14) is important. So please make sure you understand it, working out your own checks as needed.

Eq. (15) can be written more suggestively as

$$\mathcal{Z}=\prod_{\text{single particle states } i}\mathcal{Z}_i \tag{18}$$

with

$$\mathcal{Z}_i=\sum_{\text{possible occupancies } n_i}e^{-n_i\beta(\varepsilon_i-\mu)} \tag{19}$$

This factor $\mathcal{Z}_i$ is the one-state grand-canonical partition function, i.e. the grand-canonical partition function for a system with only one single-particle state, although the state can be multiply-occupied. Eq. (18) means that the full grand partition function is a product of the grand partition functions for the separate single-particle states: each degree of freedom can be excited independently. This is very powerful, since it means the probability of finding n_i particles occupying state i is completely independent of whatever else is happening. This is true at fixed μ but wouldn't be true at fixed N – try to factor Eq. (7) in this way; it doesn't work.

The grand canonical ensemble makes it very easy to write an expression for the expected occupation number of state i:

$$\langle n_i\rangle = \frac{1}{\mathcal{Z}_i}\sum_{n_i} n_i e^{-n_i\beta(\varepsilon_i-\mu)} = \frac{1}{\beta}\frac{\partial \ln\mathcal{Z}_i}{\partial\mu} \tag{20}$$

We can also express this as

$$\langle n_i\rangle = -\frac{\partial\Phi_i}{\partial\mu} \tag{21}$$

where

$$\Phi_i = -\frac{1}{\beta}\ln\mathcal{Z}_i \tag{22}$$

is the grand free energy for state i.

3.1 Non-interacting Bose gas

For a Bose system, there can be any number $n_i = 0, 1, 2, \cdots$ of bosons in a given state i. The single-state grand-canonical partition function for the state i with energy ε_i, from Eq. (19), is then

$$\mathcal{Z}_i = \sum_{n=0}^{\infty} e^{-n\beta(\varepsilon_i-\mu)} \tag{23}$$

This is a simple geometric series: there can be 0 particles, 1 particle, 2 particles, etc in the state, and so the total amount of energy in the state is an integer multiple of ε_i. Performing the sum, we find

$$\mathcal{Z}_i = \sum_{n=0}^{\infty} e^{-n\beta(\varepsilon_i-\mu)} = \frac{1}{1-e^{-\beta(\varepsilon_i-\mu)}} \tag{24}$$

The full partition function from Eq. (18) is then

$$\mathcal{Z} = \prod_i \mathcal{Z}_i = \prod_i \frac{1}{1-e^{-\beta(\varepsilon_i-\mu)}} \tag{25}$$

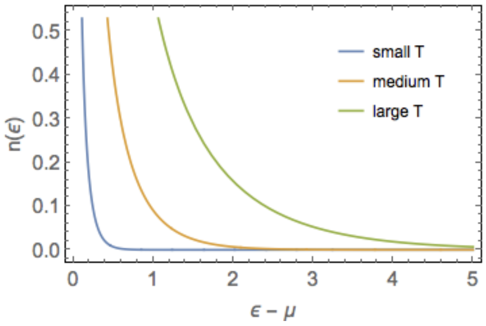
Note again that the product is over all the different states i, with ε_i the energy of that state.

The grand free energy for each state is

$$\Phi_i = -\frac{1}{\beta}\ln\mathcal{Z}_i = \frac{1}{\beta}\ln(1-e^{-\beta(\varepsilon_i-\mu)}) \tag{26}$$

Then the occupation number for each state is

$$\boxed{\langle n_i\rangle = -\frac{\partial\Phi_i}{\partial\mu} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1}} = \tag{27}$$



This is known as the **Bose-Einstein distribution**.

Note that if $\varepsilon_i < \mu$ then $\langle n_i\rangle$ is negative, which is impossible. This means that $\mu < \varepsilon_i$ for all ε_i, i.e. the chemical potential for any Bose system will be less than all of the energies. Often we set the ground state energy to zero in which case

- $\mu < 0$ for bosons

Negative chemical potential is consistent with the formula we derived in Lecture 7 for μ for a classical monatomic ideal gas: $\mu = k_B T \ln n\lambda^3 \approx -0.39\,\text{eV} < 0$ with n the number density and λ the thermal wavelength. We'll use the chemical potential for bosons in Lectures 11 and 12.

3.2 Non-interacting Fermi gas

For fermions, no two particles can occupy the same single-particle state. So the one-state grand-canonical partition function is simply

$$\mathcal{Z}_i = \sum_{n=0,1} e^{-\beta(\varepsilon_i - \mu)n} = 1 + e^{-\beta(\varepsilon_i - \mu)} \tag{28}$$

The full grand-canonical partition function is then

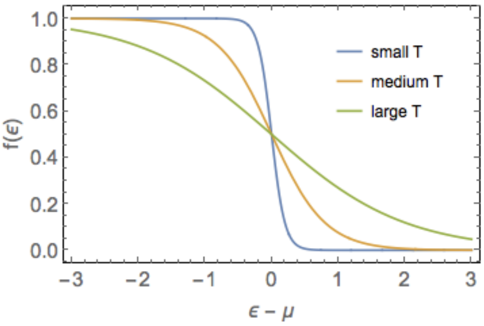
$$\mathcal{Z} = \prod_i \mathcal{Z}_i = \prod_i \left[1 + e^{-\beta(\varepsilon_i - \mu)}\right] \tag{29}$$

The grand free energy for state i is

$$\Phi_i = -\frac{1}{\beta}\ln \mathcal{Z}_i = -\frac{1}{\beta}\ln\left[1 + e^{-\beta(\varepsilon_i - \mu)}\right] \tag{30}$$

So that the occupation number for state i is

$$\boxed{\langle n_i \rangle = -\frac{\partial \Phi_i}{\partial \mu} = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1} \equiv f(\varepsilon)} = \tag{31}$$



This is known as the **Fermi-Dirac distribution** or **Fermi function**, $f(\varepsilon)$. We see that at low temperature, states with energy greater than μ are essentially unoccupied: $f(\varepsilon > \mu) \approx 0$ and states with energies less than μ are completely filled.

The chemical potential at $T = 0$ is called the **Fermi energy**, $\varepsilon_F = \mu(T = 0)$. At $T = 0$, all states below the Fermi energy are filled and the ones above the Fermi energy are empty. Thus the chemical potential for Fermi systems is positive at low temperature and corresponds to the highest occupied energy level of the system. We'll use the Fermi energy extensively to discuss fermionic systems in the quantum regime, in Lectures 13, 14 and 15.

As the temperature increases, the chemical potential decreases. This follows from $\frac{\partial \mu}{\partial T} = -\frac{S}{N}$ and $S > 0$. Eventually, the chemical potential will drop below all of the energy levels of the system. That is, it becomes negative, as with a Bose system or a classical gas.

3.3 Maxwell-Boltzmann statistics

Maxwell-Boltzmann statistics are the statistics of classical indistinguishable particles. The partition function is computed by summing over states with any particles in any state, and the sum is divided by $N!$ to account for indistinguishability. Although it is often an excellent approximation, no physical system actually obeys Maxwell-Boltzmann statistics *exactly*. Nevertheless, counting states this way turns out to be very much easier than using Bose or Fermi statistics and gives the same answer in the continuum/classical limit.

For Bose or Fermi gases, we were able to write the partition function as the product of partition functions for each state, as in Eq. (18): $\mathcal{Z}=\prod_i \mathcal{Z}_i$. With Maxwell-Boltzmann statistics, it's not clear yet if we can do this since we must divide by $N!$ where N is the *total* number of particles, not just the number of particles in state i. To avoid this subtlety, let's instead compute the grand-canonical partition function directly from the canonical partition function. Indeed, we can always write

$$\mathcal{Z}=\sum_N Z_N e^{\beta N\mu} \tag{32}$$

where Z_N is the canonical partition function with N particles. We could have tried this for Bose or Fermi statistics, but for those cases the canonical partition function Z_N with N fixed is hard to evaluate.

The canonical partition function Z_N with Maxwell-Boltzmann statistics is

$$Z_N=\frac{1}{N!}\sum_{\substack{\text{distinguishable}\\ N\text{particle microstates } k}} e^{-\beta E_k} \tag{33}$$

In this sum the particles are treated as distinguishable and indistinguishability is enforced entirely through the $N!$ factor.[3]

Since each particle is independent and the total energy E is unconstrained, we can pick any state i for any particle and therefore

$$Z_N=\frac{1}{N!}\sum_{i_1}\cdots\sum_{i_N} e^{-\beta(\varepsilon_{i_1}+\cdots+\varepsilon_{i_N})} \tag{34}$$

Here the sum over i_j is over the possible states i for particle j. Since the sums are all the same, we can simplify this as in Eq. (15):

$$Z_N=\frac{1}{N!}\left(\sum_i e^{-\beta\varepsilon_i}\right)\cdots\left(\sum_i e^{-\beta\varepsilon_i}\right)=\frac{1}{N!}Z_1^N \tag{35}$$

where the single-particle canonical partition function is

$$Z_1=\sum_i e^{-\beta\varepsilon_i} \tag{36}$$

The grand partition function for Maxwell-Boltzmann statistics is then

$$\mathcal{Z}=\sum_N \frac{1}{N!}Z_1^N e^{\beta N\mu}=\exp[Z_1 e^{\beta\mu}]=\exp\left[\sum_i e^{-\beta(\varepsilon_i-\mu)}\right]=\prod_i \exp[e^{-\beta(\varepsilon_i-\mu)}] \tag{37}$$

This has the same form as Eq. (18) after all

$$\mathcal{Z}=\prod_i \mathcal{Z}_i \tag{38}$$

with

$$\mathcal{Z}_i=\exp[e^{-\beta(\varepsilon_i-\mu)}] \tag{39}$$

In fact, if we write

$$\mathcal{Z}_i=\sum_n \frac{1}{n!}e^{-n\beta(\varepsilon_i-\mu)} \tag{40}$$

We see that $\mathcal{Z}_i$ is exactly the grand partition function for a single state using Maxwell-Boltzmann statistics.

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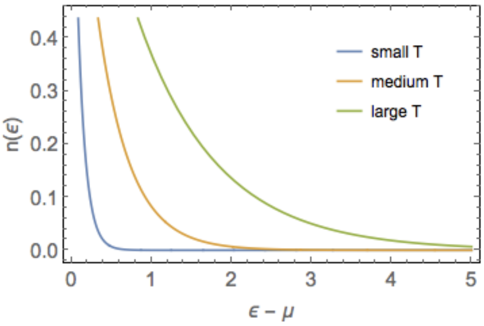
[3] Note that dividing by $N!$ is a little too much. $N!$ is the number of permutations when the particles are in different states, such as $(A,B,0)$ and $(B,A,0)$ in the table in Eq. (6). But it divides by too much when there is more than one particle in the same state, like the state $(AB,0,0)$ in the top row in the table in Eq. (6); there is only one state like this, not two. This approximation is valid when the number of accessible states is much larger than N, as at high temperature or in the classical continuum limit. In such limits, the number of configurations with more than one particle in a state is negligible.

The grand free energy for state i is then

$$\Phi_i = -\frac{1}{\beta}\ln\mathcal{Z}_i = -\frac{1}{\beta}e^{-\beta(\varepsilon_i-\mu)} \tag{41}$$

and the expected number of particles in state i is

$$\boxed{\langle n_i\rangle = -\frac{\partial\Phi_i}{\partial\mu} = e^{-\beta(\varepsilon_i-\mu)}} = \tag{42}$$



This is known as the **Maxwell-Boltzmann distribution function**. It looks a lot like the Bose-Einstein distribution function.

Unlike the Bose-Einstein case, taking $\mu \geqslant \varepsilon_i$ does not give negative occupation numbers. It can however, give occupation numbers greater than 1. When states are multiply occupied then using classical statistics is no longer justified and we must use Bose or Fermi statistics. Thus for Maxwell-Boltzmann statistics, we should have $\mu < \varepsilon_i$ for all ε_i. Or, setting the ground state energy $\varepsilon_0 = 0$ we should have $\mu < 0$. Note that this is consistent with our understanding of μ from classical statistical thermodynamics. For example, in Lecture 7 we saw that for a monatomic ideal gas with $\varepsilon_0 = 0$ then $\mu = k_B T\ln(n\lambda^3)$ with $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ the thermal wavelength. As long as we are at low density $n < \lambda^{-3}$, then $\mu < 0$. When $n \approx \lambda^{-3}$ then quantum effects become important and the sign of μ will depend on whether the gas is bosonic or fermionic, i.e. our classical computation of the monatomic ideal gas is no longer valid. We next discuss this quantum/classical transition in more detail.

4 Quantum and classical regime

Note that all of the statistics predict that the expected number of particles in state i is

$$\langle n_i\rangle = \frac{1}{e^{\beta(\varepsilon_i-\mu)} + c} \tag{43}$$

with $c = -1, 0$ or 1 for Bose-Einstein, Maxwell-Boltzmann and Fermi-Dirac statistics, respectively. The classical limit is when the probability two particles being in the same state is irrelevant. This limit requires that the $\langle n_i\rangle$ are all small, $\langle n_i\rangle \ll 1$, which, from Eq. (43) implies

$$e^{\beta(\varepsilon_i-\mu)} \gg 1 \tag{44}$$

In this limit, all the statistics gives the same results:

$$\langle n_i\rangle \approx e^{-\beta(\varepsilon_i-\mu)} \ll 1 \tag{45}$$

Let's think a little about the why the condition $e^{\beta(\varepsilon_i-\mu)} \gg 1$ is appropriate for the classical limit. Since $\beta \to \infty$ means $T \to 0$, this seems like a low temperature limit. It certainly can be a low temperature limit: taking $k_B T \ll \varepsilon$ gaurantees the state with energy ε doesn't have even one particle in it, much less two. But the classical limit can be achieved other ways as well. The key point you have to keep in mind is that while the grand canonical ensemble works at fixed μ, our intuition is for fixed N. If N is fixed, then μ is a dependent variable and has strong temperature dependence, stronger even than β. For example, recall that for a classical ideal gas (Lecture 7, Section 7.2)

$$\mu = \varepsilon_0 + k_B T\ln\frac{N}{V} - \frac{3}{2}k_B T\ln\frac{2\pi m k_B T}{h^2} - f_v k_B T\ln\frac{T}{T_v} + \cdots \tag{46}$$

where ε_0 is ground state energy, f_v are quadratic vibrational degrees of freedom, and other possible contributions are in the $\cdots$. So $\mu \sim T\ln T$ at large T when N is fixed. Therefore, for Maxwell-Boltzmann statistics at fixed N we find for a monatomic ideal gas

$$e^{-\beta(\varepsilon_i-\mu)} = \frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\left(\frac{T_v}{T}\right)^{f_v} e^{-\frac{\varepsilon_i}{k_B T}} \tag{47}$$

At large T and fixed N, this goes to zero, so that any individual single-particle state is unlikely to be multiply occupied. More physically, at high T, more and more states become accessible so it is less and less likely for any state to be multiply occupied. In addition, at high T particles are moving fast and their de Broglie wavelengths shrink: they become more like classical particles. So we can have $\langle n_i\rangle \ll 1$ either when $T\to 0$ at fixed μ or when $T\to\infty$ at fixed N. Another classical limit is $V\to\infty$ to make more and more states. There are many ways to get $\langle n_i\rangle \ll 1$.

Quite generally, increasing the temperature at fixed N decreases the chemical potential, since $\frac{\partial\mu}{\partial T} = -\frac{S}{N} < 0$. For a Bose system, $\mu < \varepsilon_i$ for all ε_i so $\varepsilon_i - \mu > 0$ and grows with temperature. In fact, it grows with temperature *faster* than β decreases with temperature: roughly $\varepsilon - \mu \sim \frac{S}{N} T \sim f T\ln T$ for some f (e.g. $S\sim N k_B \ln T$ in an ideal gas) so $\beta(\varepsilon-\mu)\sim f\ln T$ and $\langle n_i\rangle \sim \frac{1}{T^f}$ at large T. Thus we see more broadly that high temperature gives classical statistics, as you would expect, despite the fact that a superficial reading of $e^{-\beta(\varepsilon_i-\mu)} \ll 1$ makes it seem otherwise.

I suspect a number of you are cursing the chemical potential at this point. Why don't we just use the microcanonical or canonical ensembles, at fixed N, rather than the grand canonical ensemble with its unintuitive μ? As I have been saying, it is extremely difficult to use the microcanonical or canonical ensembles for Bose-Einstein of Fermi-Dirac statistics due to the challenging combinatorics of counting microstates at fixed N. As we will see, having μ around is not bad at all once you get used to it. μ is essential to understanding Bose-Einstein condensation (Lecture 12) and metals (Lectures 13 and 14).

We have seen that many limits (large T, small T, large V) lead to classical statistics. The challenge is to find a regime where the quantum statistics dominate. For quantum statistics to be relavant, we need $\langle n_i\rangle \not\ll 1$. Since the higher energy states are going to be less populated than the ground state, a reasonable condition is that $\langle n_0\rangle \approx 1$. Using Eq. (47), the ground state with $\varepsilon_i = 0$ has $\langle n_0\rangle = 1$ when

$$\frac{N}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \frac{1}{\lambda^3} \tag{48}$$

So we want $\lambda \approx \left(\frac{V}{N}\right)^{1/3}$. In other words

- **quantum statistics are important when the thermal de Broglie wavelength is of order or bigger than the interparticle spacing**

For example, at room temperature $\lambda_{\text{air}} \approx 1.87\times 10^{-11} m$ while the average interparticle spacing in air is $\left(\frac{V}{N}\right)^{1/3} = \left(\frac{k_B T}{P}\right)^{1/3} = 3\times 10^{-9}$, so particles in air are around a factor of 100 times too far for quantum effects to be important. If we keep the pressure at 1 atm, we would have to cool air to $T = 0.57K$ for quantum effects to matter.

For a classical monatomic ideal gas $\mu = k_B T\ln(\lambda^3 n)$. Thus in the classical regime when $\lambda^3\frac{N}{V} \ll 1$ the chemical potential is a large negative number, $\mu \ll 0$. As temperature is decreased at constant N and V then λ goes up and $\lambda^3 n$ increases. As $\lambda^3 n$ gets close to 1 then $\mu\to 0$ from below (more precisely, $\mu\to\varepsilon_0$ with ε_0 the ground state energy, but we usually set $\varepsilon_0 = 0$). As $\mu\to 0$, whether the system is bosonic or fermionic becomes important. For a bosonic system, μ can get closer and closer to 0, but can never reach it. As we will see in Lecture 12, as $\mu\to 0$, bosons accumulate in the ground state, a process called Bose-Einstein condensation. For a fermionic system, μ goes right through zero and ends up at a positive value the Fermi energy $\mu = \varepsilon_F > 0$ at $T = 0$. Thus the closeness of μ to 0 or equivalently the closeness of $\lambda^3 n$ to 1 indicates the onset of quantum statistics.

5 Summary

In this lecture we have seen how statistical mechanics is modified for systems of identical particles. There are three types of statistics we use

- Fermi-Dirac statistics applies to particles of half-integer spin like electrons in metals or white-dwarf stars or half-integer spin nuclei like protons or neutrons. Fermi-Dirac statistics applies not just to elementary particles, but also to atoms that have an odd number of fermions, such as ^{3}He, which comprises 2 protons, 1 neutron and 2 electrons. In Fermi-Dirac statistics, no two identical particles can occupy the same single-particle state.
- Bose-Einstein statistics applies to particles of integer spin, like photons, phonons, vibrational modes, ^{4}He atoms (=2 neutrons, 2 protons and 2 electron) or ^{95}Rb atoms (35 protons, 60 neutrons, 35 electrons). In Bose-Einstein statistics, any number of bosons can occupy the same state.
- Maxwell-Boltzmann statistics are a kind of phony classical statistics for which calculations are generally easier than with bosons or fermions. We treat the particles as all distinguishable, then throw in a factor of $\frac{1}{N!}$ to the partition function to account for indistinguishability.

The main results of this lecture were the expressions for the partition functions and probability distributions for the various statistics. We observed that for ideal gases (non-interacting particles) with any statistics, the grand-canonical partition function can be written as

$$\mathcal{Z} = \prod_{\text{single particle states } i} \mathcal{Z}_i \tag{49}$$

where $\mathcal{Z}_i$ is the grand-canonical partition function for a single state. For the various statistics we found

$$\mathcal{Z}_i = \frac{1}{1 - e^{-\beta(\varepsilon_i - \mu)}} \qquad (\text{Bose} - \text{Einstein}) \tag{50}$$

$$\mathcal{Z}_i = 1 + e^{-\beta(\varepsilon_i - \mu)} \qquad (\text{Fermi} - \text{Dirac}) \tag{51}$$

$$\mathcal{Z}_i = \exp[e^{-\beta(\varepsilon_i - \mu)}] \quad (\text{Maxwell} - \text{Boltzmann}) \tag{52}$$

From these, we deduce the probabilities $\langle n_i \rangle$ for finding n_i particles in a given state i with energy ε_i. The general formula is $\langle n_i \rangle = \frac{\partial}{\partial \mu}\left(\frac{1}{\beta}\ln \mathcal{Z}_i\right)$. We found

$$\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1} \qquad (\text{Bose} - \text{Einstein}) \tag{53}$$

$$\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1} \qquad (\text{Fermi} - \text{Dirac}) \tag{54}$$

$$\langle n_i \rangle = e^{-\beta(\varepsilon_i - \mu)} \quad (\text{Maxwell} - \text{Boltzmann}) \tag{55}$$

The general rule of thumb is that quantum statistics are relevant when states have a decent chance of being multiply occupied. At room temperature, there are so many possible states for the momenta and position of the molecules, that the chance of two being in the same state is utterly negligible. That's why classical statistical mechanics works fine most of the time. The way to find out if quantum statistics are important is to look at the thermal de Broglie wavelength

$$\lambda = \sqrt{\frac{h^2}{2\pi m k_B T}} \tag{56}$$

When the interparticle spacing $(V/N)^{1/3}$ is smaller than λ then quantum statistics is important.