Quantum gases and the grand-canonical ensemble

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References:

- Salinas, Sec 7.2 and chapter 8
- Landau, chapter 5
- Baierlein, chapter 8

Indistinguishability of quantum particles

One of the most striking differences between classical and quantum mechanics concerns the indistinguishability of particles. In classical mechanics you can always paint one particle red and the other blue. But in QM that is just not possible. Two electrons are completely indistinguishable: there is absolutely no way of telling them apart.

Let $\Psi(r_1, r_2)$ be the wave function for two identical particles. the observable quantity in $|\Psi|^2$. thus, since they are indistinguishable, we must have

$$|\Psi(r_1, r_2)|^2 = |\Psi(r_2, r_1)|^2 \tag{1}$$

This implies that the two wave-functions may differ by at most a phase factor

$$\Psi(r_2, r_1) = e^{i\theta} \Psi(r_1, r_2) \tag{2}$$

But if we flip again the two particles we must get back where we started so

$$\Psi(r_2, r_1) = e^{i\theta} \Psi(r_1, r_2) = e^{2i\theta} \Psi(r_2, r_1) \tag{3}$$

thus we must have

$$e^{2i\theta} = 1 \quad \longrightarrow \quad \begin{cases} \theta = 0 \\ \quad \text{or} \\ \theta = \pi \end{cases} \tag{4}$$

this means that we must either have

$$\psi(\vec{r_1}, \vec{r_2}) = \psi(\vec{r_2}, \vec{r_1}) \tag{5}$$

which is what we call a symmetric wave-function, or

$$\psi(\vec{r_1}, \vec{r_2}) = -\psi(\vec{r_2}, \vec{r_1}) \tag{6}$$

which is what we call an anti-symmetric wave-function.

In 1940 Wolfgang Pauli published a paper (Phys. Rev. 58, 716-722 (1940)) called "the connection between spin and statistics". There he shows, using only group theory, that the choice of symmetric or anti-symmetric wave functions depends only on the spin of the particles in question. From the theory of angular momentum one finds that spin may be either an integer or half-integer

$$\text{Spin} = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \cdots \tag{7}$$

the division found by Pauli is

Integer spin : 0, 1, 2, ... $\Rightarrow$ ψ symmetric $\Rightarrow$ Bosons

e.g. : photon, Hibbs boson, graviton, ^4He

and

Half-integer spin : $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$ $\Rightarrow$ ψ anti-symmetric $\Rightarrow$ Fermions

e.g. : protons, electrons, neutrons, ^3He

Protons, neutrons and electrons all have spin $1/2$. Helium - 4 has 2 of each, giving a total spin of 9. Hence it behaves as a Boson. But Helium - 3 has one neutron less so it's spin is $5/2$. and it behaves like a Fermion. We will learn that Bosons and Fermions behave quite differently: He4 can become superfluid but He3 cannot.

$$— \text{''} —$$

Now let us understand how this result affects the properties of a system. Consider free particles in a box and assume that they do not interact. The Hamiltonian is

$$\hat{H} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 \tag{8}$$

We have already studied this Hamiltonian before. We found that the eigen functions were plane waves (using periodic boundary condition)

$$\phi_{k}(\mathbf{r}) = \frac{e^{i \mathbf{k} \cdot \mathbf{r}}}{\sqrt{2\pi}} \tag{9}$$

where

$$k_i = \frac{2\pi l_i}{L}, \quad l_i = 0, \pm 1, \pm 2, \cdots \tag{10}$$

the energies were

$$E_k = \frac{\hbar^2 k^2}{2m} \tag{11}$$

which is simply the kinetic energy. Each quantum state is labelled by a value of k.

Now suppose we have two particles in our box, one with momentum $\hbar k_1$ and the other with momentum $\hbar k_2$. The wave function of the two particles could be

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi_{\hbar k_1}(\vec{r}_1) \phi_{\hbar k_2}(\vec{r}_2) \tag{12}$$

[If you are wondering why Ψ should be a product, recall that $|\Psi|^2$ is a probability and when the two particles are independent their joint probability must be a product].

However, this Ψ is neither symmetric nor antisymmetric. If particle 1 is a proton and particle 2 is an electron, then (12) is a perfectly fine wave-function. But if both are protons or both are electrons, then the wave-function _must_ be symmetric or anti-symmetric.

A possible symmetric wave-function may be

$$\Psi_S(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_{\hbar k_1}(\vec{r}_1) \phi_{\hbar k_2}(\vec{r}_2) + \phi_{\hbar k_1}(\vec{r}_2) \phi_{\hbar k_2}(\vec{r}_1) \right] \tag{13}$$

the first term means "1 with mom. $\hbar k_1$ and 2 with mom. $\hbar k_2$", whereas the second means "2 with mom. $\hbar k_1$ and 1 with mom. $\hbar k_2$" the factor of $1/\sqrt{2}$ is just for normalization. It is only correct if $\hbar k_1 \neq \hbar k_2$. Otherwise we would have simply

$$\Psi(\vec{r}_1, \vec{r}_2) = \phi_{\hbar k}(\vec{r}_1) \phi_{\hbar k}(\vec{r}_2) \tag{14}$$

which represents both particles with the same momentum $\hbar k$.

Similarly, we may construct an anti-symmetric wave function
as

$$\Psi_A(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left[\phi_{1k_1}(\vec{r}_1)\,\phi_{1k_2}(\vec{r}_2) - \phi_{1k_1}(\vec{r}_2)\,\phi_{1k_2}(\vec{r}_1)\right] \tag{15}$$

The physical interpretation is the same. But now $\Psi_A(\vec{r}_2, \vec{r}_1) = -\Psi_A(\vec{r}_1, \vec{r}_2)$.
If now we try to put both particles in the same quantum state
k we get zero

$$\Psi_A(\vec{r}_1, \vec{r}_1) = 0 \tag{16}$$

this is the _Pauli exclusion principle_ : two identical fermions
can never occupy the same quantum state.

So far I have ignored spin. The actual quantum state of
an electron is given by 4 quantum numbers: (k, σ), where $\sigma = \pm 1$.
Thus, we can have two electrons with momentum k, as long
as they have opposite spins. Two electrons with the same k and
the same σ is not possible by the Pauli principle.

As another illustration, consider the energy levels of an
electron in a hydrogen atom. These levels (orbitals) are
characterized by four quantum numbers $(n, \ell, m_\ell, \sigma)$.

The ground state corresponds to $n = 1, \ell = 0$ and $m_\ell = 0$.
It therefore has two possible states: $(1, 0, 0, +1)$ and $(1, 0, 0, -1)$.
In a He atom we may put one electron in each state. This
is the $1s^2$ electronic configuration.

Fock space

All we just said also generalizes to a system of N particles. But writing down these symmetrized and anti-symmetrized wave functions becomes quite cumbersome when N is large.

There is a simpler description, called the Fock space representation, where we simply say <u>how many</u> particles are in each quantum state, ignoring completely the question of <u>which</u> particle is in which.

From now on I will use the following notation:

$$j = \text{single particle state}$$
$$\text{example}: (\vec{k}, \sigma) \tag{17}$$

The Fock representation of a many particle state is then given by a set of numbers

$$\{ n_j \} = \{ n_1, n_2, \dots \} \tag{18}$$

where

$$n_j = \text{number of particles in state } j \tag{19}$$

For a bosonic system each n_j may have the values

$$\text{Bosons}: \quad n_j = 0, 1, 2, 3, \ldots \qquad (20)$$

But for Fermions the Pauli principle imposes that

$$\text{Fermions}: \quad n_j = 0, 1 \qquad (21)$$

The total number of particles in the system is specified by

$$N = \sum_j n_j \qquad (22)$$

and the total energy is

$$E = \sum_j \epsilon_j n_j \qquad (23)$$

where ϵ_j are the single particle energies (like in Eq (11)).

Contact with a heat bath

Suppose now that our system is placed in contact with a heat bath. This means that the n_j will become __random variables__ which will stay in constant fluctuations. For instance, at some given instant the bath may give a kick in a particle and increase its momentum from $\mathbb{k}$ to $\mathbb{k} + \Delta\mathbb{k}$. This means that $n_{\mathbb{k}}$ is reduced by one and $n_{\mathbb{k}+\Delta\mathbb{k}}$ is increased by 1. Hence, due to processes such as this, the numbers n_j will keep on fluctuating.

The quantity we are interested in is the joint probability distribution

$$\underline{P}(n_1, n_2, \dots) := \underline{P}(\{n_j\}) \qquad (24)$$

which gives the prob. of finding each n_j at a different number. If the system is in thermal equilibrium then we already know the answer

$$\underline{P}(\{n_j\}) = \frac{e^{-\beta E}}{Z} \qquad (25)$$

where E is given by Eq (23).

We used this same result when we discussed blackbody radiation and the photon gas. However, now there will be a fundamental difference:

$$\boxed{\text{the number of particles } N \text{ is fixed}} \qquad (26)$$

this did not happen for photons because photons can be
created and annihilated at will. But if we are talking about
a system of electrons or ^{4}He atoms, then these particles cannot
simply appear or disappear.

this means that the probabilities must be such that

$$P(\{m_j\}) = \begin{cases} \dfrac{e^{-\beta E}}{z} & \text{if } \sum_j m_j = N \\ \\ 0 & \text{otherwise} \end{cases} \tag{27}$$

the probabilities should be non-zero only for those microscopic
configurations for which the total number of particles is N.
these probabilities should then be normalized as

$$\sum_{m_1, m_2, \ldots} P(\{m_j\}) = 1 \tag{28}$$

where the sum is over all possible many-body configurations.
Inserting (27) we may also write this as

$$\frac{1}{z} \sum_{m_1, m_2, \ldots} e^{-\beta E} \delta\left(\sum_j m_j = N\right) = 1 \tag{29}$$

where $\delta(a=b)$ is the Kronecker δ (written in a slightly
different way)

$$\delta(a=b) = \begin{cases} 1 & \text{if } a = b \\ 0 & \text{if } a \neq b \end{cases} \tag{30}$$

The Grand-canonical ensemble

From (29) we may determine the partition function

$$Z = \sum_{m_1, m_2, \ldots} e^{-\beta E} \, \delta\left(\sum_j m_j = N \right) \qquad (31)$$

← See also Eq (70)

this is a <u>constrained</u> <u>sum</u>; we need to sum over an enormous number of states, but only select those which satisfy a certain constraint. Sums like this are very very difficult to handle.

Instead, we will follow a different approach. Imagine that our system is connected not only to a heat bath, but also to a <u>particle bath</u>. that is, a "bath" which may exchange particles with our system
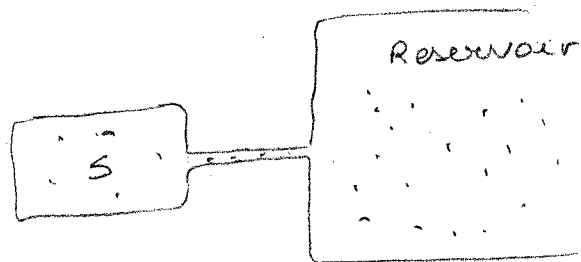
then N is no longer fixed and we will no longer have a restriction in our sum. In order for things not to get completely out of control we impose that the average number of particles be fixed at some value N

Impose:
$$\sum_j \langle m_j \rangle = N \qquad (32)$$

By doing this we are treating a completely different physical problem. However, we know from the law of large numbers that when N is large, r.v.s should not stay too far away from their average value. Hence we expect that in this case the two problems should become quite similar.

Our task now is to write down the probabilities for this different bath. This is what we call the grand-canonical ensemble.

Review of thermodynamics: the chemical potential

We saw a while ago that the first law could be written as

$$dU = TdS - pdV \tag{33}$$

This specifies the internal energy as a function of S and V. Temperature and pressure are then defined as

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad\qquad p = -\left(\frac{\partial U}{\partial V}\right)_S \tag{34}$$

If we allow for the number of particles to fluctuate, then we include in Eq (33) a term of the form

$$\boxed{dU = TdS - pdV + \mu\, dN} \tag{35}$$

where μ is called the <u>chemical potential</u>. It's physical meaning is made explicit if we write

$$\boxed{\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}} \tag{36}$$

It represents the change in energy when we introduce an additional particle in our system, at fixed volume and entropy (no heat exchanged).

U is a function of (S, V, N). It is more convenient to work with temperature instead of entropy, so we make a Legendre transformation to define the Helmholtz free energy

$$\boxed{F = U - TS} \tag{37}$$

we now have

$$dF = dU - TdS - SdT$$

$$= (TdS - pdV + \mu dN) - TdS - SdT$$

or

$$\boxed{dF = -SdT - pdV + \mu dN} \tag{38}$$

this shows that F is a function of (T, V, N). From F we may then obtain

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{39}$$

For the grand canonical ensemble, we will not work with free energy. Instead we work with the *thermodynamic potential*

$$\Phi = F - \mu N = U - TS - \mu N \tag{40}$$

we get

$$d\Phi = dF - \mu dN - N d\mu$$

$$= (-S dT - p dV + \mu dN) - \mu dN - N d\mu$$

or

$$d\Phi = -S dT - p dV - N d\mu \tag{41}$$

Thus Φ is a function of (T, V, μ). From it we may then compute

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} \qquad p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} \qquad N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \tag{42}$$

we also have an additional result which is useful when working with Φ. Start with the fact that U is a homogeneous function of (S, V, N):

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \tag{43}$$

Now differentiate both sides with respect to λ:

$$\frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} +$$

$$+ \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = \frac{\partial}{\partial \lambda}\left[\lambda U(S, V, N)\right]$$

But from (34)

$$\frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} = T$$

and similarly for the other two terms. We therefore conclude that

$$\boxed{TS - pV + \mu N = U} \tag{44}$$

which is known as Euler's equation. Going back now to (40) we conclude that

$$\boxed{\Phi = -pV} \tag{45}$$

This gives an easy way of computing the equation of state from Φ.

Equilibrium is the minimum of the thermodynamic potential

We saw that the canonical ensemble was the state which minimizes the free energy $F = U - TS$. But now the number of particles may also fluctuate, so equilibrium must be obtained from a competition of U, $-TS$ and the energy cost imbued in changing the number of particles, which is $-\mu N$. Thus, in the grand canonical ensemble, equilibrium will be the state which minimizes the thermodynamic potential

$$\Phi = U - TS - \mu N \tag{46}$$

Our system is described by the probabilities $P(\{m_j\})$ so

$$U = \sum_{\{m_j\}} \left(\sum_j \epsilon_j m_j \right) P(\{m_j\}) \tag{47a}$$

$$S = - k_B \sum_{\{m_j\}} P(\{m_j\}) \ln P(\{m_j\}) \tag{47b}$$

$$N = \sum_{\{m_j\}} \left(\sum_j m_j \right) P(\{m_j\}) \tag{47c}$$

so

$$\Phi = \sum_{\{m_j\}} \left[\left(\sum_j (\epsilon_j - \mu) m_j \right) + k_B T \ln P(\{m_j\}) \right] P(\{m_j\}) \tag{48}$$

But, as before, this minimization must be subjected to the constraint that the probabilities are normalized to 1.

This we should normalize instead

$$\Phi' = \Phi + \alpha \left(1 - \sum_{\{m_j\}} P(\{m_j\}) \right) \tag{49}$$

where α is a Lagrange multiplier. then, the condition

$$\frac{\partial \Phi'}{\partial \alpha} = 0 \quad \leadsto \quad 1 - \sum_{\{m_j\}} P(\{m_j\}) = 0 \tag{50}$$

which fixes the normalization.

the other equations are

$$\frac{\partial \Phi'}{\partial P(\{m_j\})} = \sum_j (\epsilon_j - \mu) m_j + k_B T \ln P(\{m_j\}) + \overbrace{k_B T}^{\text{const}} - \alpha = 0$$

this implies that

$$\ln P(\{m_j\}) = -\frac{\sum_j (\epsilon_j - \mu) m_j}{k_B T} + \text{const}$$

and

$$P(\{m_j\}) = \text{const} \times e^{-\sum_j (\epsilon_j - \mu) m_j / k_B T}$$

The normalization constant is

$$Q = \sum_{\{M_j\}} e^{-\sum_j (\epsilon_j - \mu) M_j / k_B T}$$

(51)

which is called the grand canonical partition function. then we may finally write

$$P(\{M_j\}) = \frac{e^{-\sum_j (\epsilon_j - \mu) M_j / k_B T}}{Q}$$

(52)

That's it: we have just found the grand canonical probabilities from minimizing the thermodynamic potential.

Now let's go back to (48) and find what is Φ at this minimum. we have

$$\ln P(\{M_j\}) = \frac{-\sum_j (\epsilon_j - \mu) M_j}{k_B T} - \ln Q$$

so

$$\Phi = \sum_{\{M_j\}} \left[\sum_j (\epsilon_j - \mu) M_j - k_B T \frac{\sum_j (\epsilon_j - \mu) M_j}{k_B T} - k_B T \ln Q \right] P(\{M_j\})$$

$$= -k_B T \ln Q \underbrace{\sum_{\{M_j\}} P(\{M_j\})}_{1}$$

thus we conclude that

$$\Phi = -k_B T \ln Q \qquad (53)$$

this is the analog of $F = -k_B T \ln Z$, but for the Grand canonical case.

Note also how the probabilities (52) for the different quantum states are statistically independent

$$P(\{m_j\}) = P(m_1, m_2, \ldots, m_j, \ldots) = P(m_1) P(m_2) \ldots P(m_j) \ldots \qquad (54)$$

where

$$P(m_j) = \frac{e^{-\beta(\epsilon_j - \mu) m_j}}{Q_j} \qquad (55)$$

and

$$Q_j = \sum_{m_j} e^{-\beta(\epsilon_j - \mu) m_j} \qquad (56)$$

Bosons and Fermions

Recall that, according to the spin-statistics theorem of W. Pauli, we should have

Bosons: $M_j = 0, 1, 2, 3, \ldots$

Fermions: $M_j = 0, 1$.

The GC partition function (51) may be written as

$$Q = \prod_j \left(\sum_{M_j} e^{-\beta(\epsilon_j - \mu) M_j} \right)$$

$$= \prod_j \left(\sum_{M_j} x^{M_j} \right) \qquad x = e^{-\beta(\epsilon_j - \mu)}$$

For Fermions we get

$$\sum_{M_j = 0, 1} x^{M_j} = 1 + x = 1 + e^{-\beta(\epsilon_j - \mu)}$$

Thus, for Fermions

$$\boxed{Q_F = \prod_j \left[1 + e^{-\beta(\epsilon_j - \mu)} \right]} \qquad \text{(Fermions)} \qquad (54)$$

the thermodynamic potential (53) then becomes

$$\boxed{\Phi_F = -k_B T \sum_j \ln \left(1 + e^{-\beta(\epsilon_j - \mu)} \right)} \qquad \text{(Fermions)} \qquad (55)$$

For Bosons, on the other hand

$$\sum_{M_j=0}^{\infty} x^{M_j} = \frac{1}{1-x} = \frac{1}{1-e^{-\beta(\epsilon_j - \mu)}}$$

Thus

$$Q_B = \prod_j \left[\frac{1}{1 - e^{-\beta(\epsilon_j - \mu)}} \right] \qquad \text{(Bosons)} \qquad (56)$$

and

$$\Phi_B = k_B T \sum_j \ln\left(1 - e^{-\beta(\epsilon_j - \mu)}\right) \qquad (57)$$

Fermi-Dirac and Bose-Einstein

Let us compute the average number of particles at state j: we may use the individual $P(M_j)$ instead of $P(\{M_j\})$. Thus

$$\overline{M_j} = \langle M_j \rangle = \sum_{M_j} M_j \, P(M_j) = \sum_{M_j} M_j \, \frac{e^{-\beta(\epsilon_j - \mu) M_j}}{Q_j}$$

we may write this as

$$\langle \overline{M_j} \rangle = \frac{1}{Q_j} \left(- \frac{\partial}{\partial(\beta\epsilon_j)} \sum_{M_j} e^{-\beta(\epsilon_j - \mu) M_j} \right)$$

or

$$\overline{M_j} = - \frac{\partial}{\partial(\beta\epsilon_j)} \ln Q_j \tag{58}$$

For Fermions Eq (54) gives

$$\overline{M_j} = - \frac{\partial}{\partial(\beta\epsilon_j)} \ln \left(1 + e^{-\beta(\epsilon_j - \mu)} \right)$$

$$= \frac{e^{-\beta(\epsilon_j - \mu)}}{1 + e^{-\beta(\epsilon_j - \mu)}}$$

or

$$\boxed{\overline{M_j} = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}} \qquad \text{(Fermions)} \tag{59}$$

This is called the Fermi-Dirac distribution.

For Bosons Eq (56) gives

$$\overline{m}_j = -\frac{\partial}{\partial(\beta \epsilon_j)} \ln \left[\frac{1}{1 - e^{-\beta(\epsilon_j - \mu)}} \right]$$

$$= \frac{\partial}{\partial(\beta \epsilon_j)} \ln \left(1 - e^{-\beta(\epsilon_j - \mu)} \right)$$

$$= \frac{e^{-\beta(\epsilon_j - \mu)}}{1 - e^{-\beta(\epsilon_j - \mu)}}$$

thus we get

$$\boxed{\overline{m}_j = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}}$$ (60)

This is called the Bose-Einstein distribution

Summary of useful formulas

$$\Phi = F - \mu N = U - TS - \mu N = -pV$$

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_{T,\mu} \qquad N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

Bosons

$$\Phi = k_B T \sum_j \ln\left(1 - e^{\beta(\epsilon_j - \mu)}\right)$$

$$\overline{m}_j = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}$$

Fermions

$$\Phi = -k_B T \sum_j \ln\left(1 + e^{-\beta(\epsilon_j - \mu)}\right)$$

$$\overline{m}_j = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}$$

$$N = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = \sum_j \overline{m}_j$$

The classical limit

We must be able, somehow, to recover classical results from our formalism. By "classical", what we mean is a situation where this distinction between Fermions and Bosons becomes unimportant.

We may write the results for Bosons and Fermions together as

$$\Phi = \pm k_B T \sum_j \ln\left(1 \mp e^{-\beta(\epsilon_j - \mu)}\right) \tag{61}$$

$$\overline{m}_j = \frac{1}{e^{\beta(\epsilon_j - \mu)} \mp 1} \tag{62}$$

where the upper sign is for Bosons and the lower sign for Fermions.

Looking at these formulas we see that the $\pm$ signs will vanish when

$$e^{\beta(\epsilon_j - \mu)} \gg 1 \tag{63}$$

In this case (62) becomes

$$\overline{m}_j \simeq \frac{1}{e^{\beta(\epsilon_j - \mu)}} = e^{-\beta(\epsilon_j - \mu)} \tag{64}$$

For (61) we may use the Taylor expansion

$$\ln(1 \pm x) \simeq \pm x \tag{65}$$

We then get

$$\Phi \simeq \pm k_B T \sum_j \left(\mp e^{-\beta(\epsilon_j - \mu)} \right)$$

or

$$\Phi \simeq - k_B T \sum_j e^{-\beta(\epsilon_j - \mu)} \qquad (66)$$

Now let's try to understand what these results mean. First, we use Eq (42) to compute

$$N = - \left(\frac{\partial \Phi}{\partial \mu} \right) = \sum_j e^{-\beta(\epsilon_j - \mu)} \qquad (67)$$

we then see that

$$\frac{\overline{m}_j}{N} = \frac{e^{-\beta(\epsilon_j - \mu)}}{\sum_j e^{-\beta(\epsilon_j - \mu)}} =$$

Or, cancelling out the terms $e^{\beta \mu}$,

$$\frac{\overline{m}_j}{N} \simeq \frac{e^{-\beta \epsilon_j}}{\sum_j e^{-\beta \epsilon_j}} \qquad (68)$$

this is the Maxwell - Boltzmann distribution. We may interpret $\overline{m}_j / N$ as the probability of finding state j occupied. this is then simply the Gibbs formula

the classical limit therefore appears naturally as the situation where the prob. of having a particle occupying a given state is small. If that is the case, then indistinguishibility becomes irrelevant because you almost never encounter two particles in the same state.

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Now let us go all the way back to the canonical ensemble. In Eq (31) we wrote down the partition function as

$$Z(N) \sum_{\{M_j\}} e^{-\beta E} \delta\left(\sum_j M_j = N\right) \qquad (69)$$

which, if you recall, was related to the constraint that in the canonical ensemble the number of particles is fixed. Recall also that $E = \sum_j \epsilon_j M_j$.

If $N = 1$ we get

$$Z_1 = e^{-\beta \epsilon_1} + e^{-\beta \epsilon_2} + \cdots = \sum_j e^{-\beta \epsilon_j} \qquad (70)$$

this is simply the partition function of a single non-interacting particle.

Suppose now that $N=2$. In this case we must distinguish between Bosons and Fermions. For Bosons

$$Z(2) = e^{-\beta(\epsilon_1 + \epsilon_1)} + e^{-\beta(\epsilon_1 + \epsilon_2)} + e^{-\beta(\epsilon_1 + \epsilon_3)} + \cdots$$

$$+ e^{-\beta(\epsilon_2 + \epsilon_2)} + e^{-\beta(\epsilon_2 + \epsilon_3)} + \cdots$$

Note that this is <u>not</u> $(Z_1)^2$ because Z_1^2 would have $e^{-\beta(\epsilon_1 + \epsilon_2)}$ and $e^{-\beta(\epsilon_2 + \epsilon_1)}$.

If we keep going things just get more and more complicated. This is why we gave up on the canonical ensemble and went instead to the grand canonical case.

What I want to do now in connect the canonical partition function $Z(N)$ with the Grand-canonical function Q. We have

$$Z(N) = \sum_{\{M_j\}} e^{-\beta E} \delta\left(\sum_j M_j = N\right)$$ (7.1)

$$Q = \sum_{\{M_j\}} e^{-\beta \sum_j (\epsilon_j - \mu) M_j}$$ (7.2)

the canonical function $Z(N)$ is a constrained sum, which picks only those states in which the total number of particles is N.

The connection between the two functions can be made as follows. Let

$$\delta = e^{\beta \mu}$$ (7.3)

which, for historical reasons, is called the fugacity. We now write (7.2) as

$$Q = \sum_{\{M_j\}} \delta^{\sum_j M_j} e^{-\beta \sum_j \epsilon_j M_j}$$

The trick is now to split this as a sum of constrained sums for each value of N.

$$Q = \sum_{N=0}^{\infty} \mathcal{Z}^N \underbrace{\sum_{\{M_j\}} \bar{e}^{\phi \sum_j \epsilon_j M_j} \, \delta\left(\sum_j \epsilon_j = N\right)}_{Z(N)}$$

Thus we conclude that

$$\boxed{Q = \sum_{N=0}^{\infty} \mathcal{Z}^N \, Z(N)}$$

(74)

the function $Q(\mathcal{Z})$ is the <u>generating function</u> of $Z(N)$ because if you know $Q(\mathcal{Z})$ you may find $Z(N)$ by a Taylor series expansion (just like the characteristic function in probability theory)

As a particular case, consider the classical limit. There we saw in Eq (66) that

$$\Phi \simeq -\frac{1}{\beta} \sum_j e^{-\beta(\epsilon_j - \mu)}$$

$$= -\frac{1}{\beta} e^{\beta\mu} \sum_j e^{-\beta\epsilon_j}$$

$$= -\frac{1}{\beta} \beta z_1$$

But   (75)

$$\Phi = -\frac{1}{\beta} \ln Q \quad \leadsto \quad Q = e^{-\beta\Phi}$$

Thus   (76)

$$Q \simeq e^{\beta z_1}$$

Expanding in a Taylor series we get

$$Q = \sum_{N=0}^{\infty} \frac{\beta^N z_1^N}{N!}$$ (77)

Comparing with (74) we therefore conclude that

$$\boxed{Z(N) = \frac{z_1^N}{N!}}$$ (78)

In this formalism the N-particle partition function already naturally contains the correct Boltzmann counting $1/N!$

This makes sense: in the Fock representation we don't care *which* particle is in which state. All we care about is *how many* particles are in each state. Thus, indistinguishability is built into the theory, and so must also the correct Boltzmann counting.

First quantum correction to an ideal gas

Let us now consider an ideal gas. This means that the quantum states j are actually of the form (k, s), where s is the spin state. I will assume a more general situation where the total spin S can be either an integer (Bosons) or half-integer (Fermions). the quantity s then takes on $2S+1$ values

$$s = S, S-1, \ldots, -S+1, -S \qquad (2S+1 \text{ in total}). \qquad (79)$$

we will assume there are no magnetic fields present, so the energy depends only on k and reads

$$\epsilon_k = \frac{\hbar^2 k^2}{2m} \qquad (80)$$

the number of particles in the state $j = (k, s)$ is

$$\overline{m}_{k,s} = \frac{1}{e^{\beta(\epsilon_k - N)} \pm 1} \qquad (81)$$

with + for Fermions and − for Bosons.

The total number of particles in a volume medium is

$$N = \sum_{k,s} \overline{m}_{k,s} \tag{82}$$

and the total energy is

$$U = \sum_{k,s} \epsilon_k \, \overline{m}_{k,s} \tag{83}$$

we may transform these sums into integrals by introducing the density of states. Recall that if $f(\epsilon_k)$ is an arbitrary function of energy then

$$\sum_{k,s} f(\epsilon_k) = (2s+1) \frac{V}{(2\pi)^3} \int d^3k \; f(\epsilon_k)$$

$$= (2s+1) \frac{V}{(2\pi)^3} \, 4\pi \int dk \; k^2 \, f(\epsilon_k)$$

Now let

$$\epsilon = \frac{\hbar^2 k^2}{2m} \quad \leadsto \quad k = \frac{\sqrt{2m}}{\hbar} \sqrt{\epsilon_k}$$

$$dk = \frac{\sqrt{2m}}{\hbar} \frac{1}{2\sqrt{\epsilon_k}} d\epsilon$$

$$k^2 dk = \frac{(2m)^{3/2}}{2\hbar^3} \sqrt{\epsilon_k} \, d\epsilon$$

thus

$$\sum_{k,s} f(\epsilon_k) = (2S+1) \frac{V}{(2\pi)^3} 4\pi \frac{(2m)^{3/2}}{2\hbar^3} \int d\epsilon \, f(\epsilon) \sqrt{\epsilon}$$

we then define the density of states as

$$\boxed{D(\epsilon) = V \frac{(2S+1)}{4\pi^2 \hbar^3} (2m)^{3/2} \sqrt{\epsilon}} \qquad (84)$$

To be more succinct, let us write

$$\boxed{D(\epsilon) = \alpha V \sqrt{\epsilon} \,, \qquad \alpha = \frac{(2S+1)(2m)^{3/2}}{4\pi^2 \hbar^3}} \qquad (85)$$

Returning now to (82) and (83), we may write

$$N = \int_0^\infty d\epsilon \, D(\epsilon) \, \overline{m}(\epsilon) \qquad (86)$$

$$U = \int_0^\infty d\epsilon \, D(\epsilon) \, \epsilon \, \overline{m}(\epsilon) \qquad (87)$$

Later on we will consider these integrals in more detail, for both Bosons and Fermions. For now I want to look only at the first quantum correction.

Recall from (63) that in the classical limit $e^{\beta(\epsilon - \mu)} \gg 1$. we therefore write

$$\bar{n}(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} \pm 1} = e^{-\beta(\epsilon - \mu)} \frac{1}{1 \pm e^{-\beta(\epsilon - \mu)}}$$

then, since $e^{-\beta(\epsilon - \mu)} \ll 1$ we may expand

$$\frac{1}{1 \pm x} \simeq 1 \mp x$$

To get

$$\bar{n}(\epsilon) \simeq e^{-\beta(\epsilon - \mu)} \left[1 \mp e^{-\beta(\epsilon - \mu)} \right]$$

The upper sign is for Fermions and the lower for Bosons.

$$\bar{n}(\epsilon) = e^{-\beta(\epsilon - \mu)} \mp e^{-2\beta(\epsilon - \mu)} \tag{88}$$

The total number of particles, Eq (86), becomes

$$N = \alpha V \int_0^\infty d\epsilon \sqrt{\epsilon} \left\{ e^{-\beta(\epsilon - \mu)} \mp e^{-2\beta(\epsilon - \mu)} \right\}$$

$$= \alpha V \left\{ e^{\beta\mu} \underbrace{\int_0^\infty d\epsilon \sqrt{\epsilon} \, e^{-\beta\epsilon}}_{\frac{\sqrt{\pi}}{2 \beta^{3/2}}} \mp e^{2\beta\mu} \underbrace{\int_0^\infty d\epsilon \sqrt{\epsilon} \, e^{-2\beta\epsilon}}_{\frac{\sqrt{\pi}}{2(2\beta)^{3/2}}} \right\}$$

$$N = \alpha V \frac{\sqrt{\pi}}{2} (k_B T)^{3/2} \left\{ e^{\beta\mu} \mp \frac{e^{2\beta\mu}}{2^{3/2}} \right\}$$

Let us simplify our constants:

$$\alpha \frac{\sqrt{\pi}}{2} = \frac{(2S+1)(2m)^{3/2}}{4\pi^2 \hbar^3} \frac{\sqrt{\pi}}{2}$$

$$= (2S+1) \frac{(2m)^{3/2}}{8\pi^{3/2} \hbar^3}$$

$$= (2S+1) \left(\frac{2m}{2^2 \pi \hbar^2} \right)^{3/2}$$

$$= (2S+1) \left(\frac{m}{2\pi \hbar^2} \right)^{3/2}$$

we then get

$$N = (2S+1) \left(\frac{m k_B T}{2\pi \hbar^2} \right)^{3/2} V \left\{ e^{\beta\mu} \mp \frac{e^{2\beta\mu}}{2^{3/2}} \right\}$$

We now introduce a new quantity called the thermal de Broglie wave length

$$\lambda = \sqrt{\frac{2\pi \hbar^2}{m k_B T}} \qquad (89)$$

We then get

$$N = \frac{(2S+1)V}{\lambda^3}\left\{ e^{\beta \mu} \mp \frac{e^{2\beta \mu}}{2^{3/2}}\right\} \qquad (90)$$

this equation actually fixes the chemical potential μ

$$e^{\beta \mu} \mp \frac{e^{2\beta \mu}}{2^{3/2}} = \frac{\lambda^3 N/V}{(2S+1)} \qquad (91)$$

or

$$z \mp \frac{z^2}{2^{3/2}} = \frac{\lambda^3 N/V}{(2S+1)} \qquad (92)$$

Recall that in the classical limit $z = e^{\beta \mu} \ll 1$. Thus the first order solution will be

$$e^{\beta \mu} = z = \frac{\lambda^3 N/V}{(2S+1)} \qquad (93)$$

or

$$\beta \mu = \ln\left\{ \frac{\lambda^3 N/V}{(2S+1)}\right\} \qquad (94)$$

This fixes the chemical potential as a function of the temperature and the density N/V. Note that the condition for $e^{\beta\mu}$ to be small may be written as

$$\lambda^3 N/V \ll 1$$

or

$$\boxed{\frac{N}{V} \ll \frac{1}{\lambda^3}}$$ $\left(\begin{array}{c}\text{condition for the}\\\text{classical limit}\end{array}\right)$ (95)

This has an important physical interpretation: V/N is the typical volume occupied by each particle and λ is the typical wavelength of the quantum wave packets. According to (95) the classical limit will hold when the density of particles N/V is much smaller than the typical length of quantum effects.

Note also that when $\lambda^3 N/V < 1$ (ie, in the classical limit), we will have

$$\mu < 0 \qquad (96)$$

since $\ln(x) < 0$ for $x < 1$. In the classical limit the chemical potential is negative.

Now let us determine the first quantum correction to μ.
We may simply solve Eq (92), which is quadratic in z.
But since we only want an approximate solution, we may
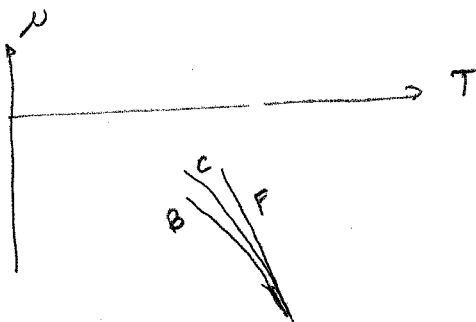substitute the classical result for z^2:

$$z = \frac{\lambda^3 N/V}{(2S+1)} \pm \frac{z^2}{2^{3/2}}$$

$$\approx \frac{\lambda^3 N/V}{(2S+1)} \pm \frac{1}{2^{3/2}} \left[\frac{\lambda^3 N/V}{2S+1} \right]^2$$

thus

$$\boxed{\beta\mu \approx \ln \left\{ \frac{\lambda^3 N/V}{(2S+1)} \left[1 \pm \frac{1}{2^{3/2}} \frac{\lambda^3 N/V}{(2S+1)} \right] \right\}} \qquad (97)$$

Note that for Fermions the chemical potential is larger than
the classical case, whereas for Bosons it is smaller

Next we look at the energy, Eq (87). We have

$$U = \alpha V \int_0^\infty d\epsilon \; \epsilon^{3/2} \; \bar{n}(\epsilon) \qquad\qquad (97')$$

$$= \alpha V \int_0^\infty d\epsilon \; \epsilon^{3/2} \left\{ e^{-\beta(\epsilon - \mu)} \mp e^{-2\beta(\epsilon - \mu)} \right\}$$

$$= \alpha V \left\{ e^{\beta\mu} \; \frac{3\sqrt{\pi}}{4\,\beta^{5/2}} \mp e^{2\beta\mu} \; \frac{3\sqrt{\pi}}{4(2\beta)^{5/2}} \right\}$$

$$= \frac{3}{2} \underbrace{\left(\frac{\alpha\sqrt{\pi}}{2\beta^{3/2}} \right)}_{\dfrac{(2S+1)}{\lambda^3}} \frac{V}{\beta} \left\{ e^{\beta\mu} \mp \frac{e^{2\beta\mu}}{2^{5/2}} \right\}$$

Now we need to be careful. If we want the result correct to second order in μ, we must use the second order solution of (97). Let

$$a = \frac{\lambda^3 N/V}{(2S+1)}$$

Then we write

$$U = \frac{3}{2} N k_B T \; \frac{1}{a} \left\{ e^{\beta\mu} \mp \frac{e^{2\beta\mu}}{2^{5/2}} \right\}$$

and

$$e^{\beta\mu} \approx a \pm \frac{a^2}{2^{3/2}}$$

Then

$$e^{2\beta\mu} = \left(a \pm \frac{a^2}{2^{3/2}}\right)^2 \simeq a^2$$

thus

$$e^{\beta\mu} \mp \frac{e^{2\beta\mu}}{2^{5/2}} \simeq a \pm \frac{a^2}{2^{3/2}} \mp \frac{a^2}{2^{5/2}}$$

$$= a \pm \frac{a^2}{2^{3/2}}\left(1 - \frac{1}{2}\right)$$

$$= a \pm \frac{a^2}{2^{5/2}}$$

thus

$$U = \frac{3}{2}Nk_BT \; \frac{1}{a}\left(a \pm \frac{a^2}{2^{5/2}}\right)$$

or

$$U \simeq \frac{3}{2}Nk_BT\left\{1 \pm \frac{1}{2^{5/2}} \; \frac{\lambda^3 N/V}{(2S+1)}\right\} \qquad (98)$$

The Pauli exclusion principle increases the energy of a system, whereas for Bosons the energy decreases.

what is most remarkable about this result is that Fermions and Bosons at the same temperature will have different kinetic energies: recall that there is no interaction, so the energy is purely kinetic. Quantum effects break equipartition

Thus, if we have a mixture of ^{3}He and ^{4}He, both at the same temperature, the average kinetic energy of a ^{3}He atom will be higher due to quantum effects.

$$-\mathrm{i}\!\!-$$

Finally, let us look at the thermodynamic potential

$$\Phi = \mp k_B T \sum_{k,\,s} \ln\left[1 \pm e^{-\beta(\epsilon-\mu)}\right] \qquad (??)$$

$$= \mp k_B T \,\alpha V \int_0^\infty d\epsilon\, \sqrt{\epsilon}\, \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) \qquad (99)$$

Now we integrate by parts.

$$u = \ln\left(1 \pm e^{-\beta(\epsilon-\mu)}\right) \quad\leadsto\quad du = \frac{\pm(-\beta)\,e^{-\beta(\epsilon-\mu)}}{1 \pm e^{-\beta(\epsilon-\mu)}}\, d\epsilon$$

$$= \frac{\mp \beta}{e^{\beta(\epsilon-\mu)} \pm 1}\, d\epsilon$$

$$= \mp \beta \bar{n}(\epsilon)\, d\epsilon$$

$$dv = \sqrt{\epsilon}\, d\epsilon \quad\leadsto\quad v = \frac{2}{3}\epsilon^{3/2}$$

the cross term is

$$\frac{2}{3}\epsilon^{3/2}\,(\mp\beta)\,\bar{n}(\epsilon)\Big|_0^\infty = 0$$