

Quantum gases and the grand-canonical ensemble

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References:

- Salinas, Sec 7.2 and chapter 8
- Landau, chapter 5
- Baisellein, 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 is $|\psi|^2$. Thus, since they are indistinguishable, we must have

$$|\psi(r_1, r_2)|^2 = |\psi(r_2, r_1)|^2 \quad (1)$$

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

$$\psi(r_2, r_1) = e^{i\theta} \psi(r_1, r_2) \quad (2)$$

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

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

thus we must have

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

this means that we must either have indistinguishable particles

$$\Psi(r_1, r_2) = \Psi(r_2, r_1) \quad (5)$$

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

$$\Psi(r_1, r_2) = -\Psi(r_2, r_1) \quad (6)$$

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

$$\text{Spin} = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \dots \quad (7)$$

the division found by Pauli is

Integer spin: $0, 1, 2, \dots \Rightarrow \Psi$ symmetric \Rightarrow Bosons

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

Half-integer spin: $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots \Rightarrow \Psi$ 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 0. Hence it behaves as a Boson. But Helium-3 has one neutron less so its spin is $1/2$ and it behaves like a Fermion. We will learn that Bosons and Fermions behave quite differently: He4 can become superfluid but He3 cannot.

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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

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

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

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

where

$$\mathbf{k}_i = \frac{2\pi \mathbf{l}_i}{L}, \quad \mathbf{l}_i = 0, \pm 1, \pm 2, \dots \quad (10)$$

the energies were

$$E_{\mathbf{k}} = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad (11)$$

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

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

$$\Psi(r_1, r_2) = \phi_{k_1}(r_1) \phi_{k_2}(r_2) \quad (12)$$

[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

$$\Psi_S(r_1, r_2) = \frac{1}{\sqrt{2}} \left[\phi_{k_1}(r_1) \phi_{k_2}(r_2) + \phi_{k_1}(r_2) \phi_{k_2}(r_1) \right] \quad (13)$$

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

$$\Psi(r_1, r_2) = \phi_k(r_1) \phi_k(r_2), \quad (14)$$

which represents both particles with the same momentum k .

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

$$\Psi_A(r_1, r_2) = \frac{1}{\sqrt{2}} \left[\phi_{l_1}(r_1) \phi_{l_2}(r_2) - \phi_{l_1}(r_2) \phi_{l_2}(r_1) \right] \quad (15)$$

The physical interpretation is the same. But now $\Psi_A(r_2, r_1) = -\Psi_A(r_1, r_2)$. If now we try to put both particles in the same quantum state l_1 we get zero

$$\Psi_A(r_1, r_1) = 0 \quad (16)$$

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: (l, σ) , where $\sigma = \pm 1$. Thus, we can have two electrons with momentum l , as long as they have opposite spins. Two electrons with the same l 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, l, m_l, σ) .

The ground state corresponds to $n=1, l=0$ and $m_l=0$. 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 how many particles are in each quantum state, ignoring completely the question of which particle is in which.

From now on I will use the following notation:

j = single particle state
example: $(1k, \sigma)$

(17)

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

$$\{m_j\} = \{m_1, m_2, \dots\}$$

(18)

where

$$m_j = \text{number of particles in state } j$$

(19)

For a bosonic system each n_j may have the values

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

But for Fermions the Pauli principle imposes that

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

The total number of particles in the system is specified by

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

and the total energy is

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

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 nk to $nk + \Delta nk$. This means that n_{nk} is reduced by one and $n_{nk + \Delta nk}$ 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

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

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

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

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:

the number of particles N is fixed

(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 ${}^4\text{He}$ atom, then these particles cannot simply appear or disappear.

This means that the probabilities must be such that

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

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

$$\sum_{m_1, m_2, \dots} P(\{m_j\}) = 1 \quad (28)$$

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

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

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

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

The Grand-canonical ensemble

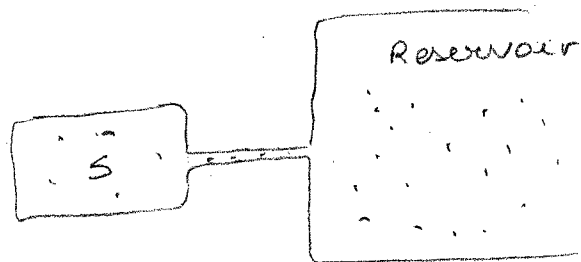
From (29) we may determine the partition function

$$Z = \sum_{M_1, M_2, \dots} e^{-\beta E} \delta\left(\sum_j M_j = N\right) \quad (31)$$

← See also Eq (70)

this is a constrained sum; 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 particle bath. 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: $\sum_j \langle m_j \rangle = N \quad (32)$

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

$$dU = Tds - pdV \quad (33)$$

this specifies the internal energy as a function of S and V .

Temperature and pressure are then defined as

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad P = - \left(\frac{\partial U}{\partial V} \right)_S \quad (34)$$

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

$$dU = Tds - pdV + \mu dN \quad (35)$$

where μ is called the chemical potential. Its physical meaning is made explicit if we write

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

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

$$F = U - TS \quad (37)$$

we now have

$$\begin{aligned} dF &= dU - Tds - SdT \\ &= (Tds - pdv + \mu dN) - Tds - SdT \end{aligned}$$

or

$$dF = -SdT - pdv + \mu dN \quad (38)$$

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

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

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

$$\Phi = F - \mu N = U - TS - \mu N \quad (40)$$

we get

$$\begin{aligned} d\Phi &= dF - \mu dN - N d\mu \\ &= (-S dT - p dV + \mu dN) - \mu dN - N d\mu \end{aligned}$$

or

$$d\Phi = -S dT - p dV - N d\mu \quad (41)$$

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

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

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) :

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \quad (43)$$

Now differentiate both sides with respect to λ :

$$\begin{aligned} \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \\ + \frac{\partial U(\lambda S, \lambda V, \lambda N)}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = \frac{\partial}{\partial \lambda} [\lambda U(S, V, N)] \end{aligned}$$

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

$$\boxed{TS - pV + \mu N = U} \quad (44)$$

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

$$\boxed{\Phi = -pV} \quad (45)$$

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 involved 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

$$\Phi = U - TS - \mu N \quad (46)$$

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

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

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

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

so

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

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

1.

Thus we should normalize instead

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

where α is a Lagrange multiplier. Then, the condition

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

which fixes the normalization.

The other equations are

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

This implies that

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

and

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

The normalization constant is

$$Q = \sum_{\{M_j\}} e^{-\sum_j (\epsilon_j - \mu) M_j / k_B T} \quad (51)$$

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

$$P(\{M_j\}) = \frac{e^{-\sum_j (\epsilon_j - \mu) M_j / k_B T}}{Q} \quad (52)$$

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

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

so

$$\begin{aligned} \Phi &= \sum_{\{M_j\}} \left[\sum_j (\epsilon_j - \mu) M_j - k_B T \sum_j \frac{(\epsilon_j - \mu) M_j}{k_B T} - k_B T \ln Q \right] P(\{M_j\}) \\ &= -k_B T \ln Q \underbrace{\sum_{\{M_j\}} P(\{M_j\})}_1 \end{aligned}$$

Thus we conclude that

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

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

$$P(\{m_j\}) = P(m_1, m_2, \dots, m_j, \dots) = P(m_1)P(m_2)\dots P(m_j)\dots \quad (54)$$

where

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

and

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

Bosons and Fermions

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

$$\text{Bosons: } m_j = 0, 1, 2, 3, \dots$$

$$\text{Fermions: } m_j = 0, 1.$$

the GC partition function (51) may be written as

$$\begin{aligned} Q &= \prod_j \left(\sum_{m_j} e^{-\beta(\epsilon_j - \mu)m_j} \right) \\ &= \prod_j \left(\sum_{m_j} x^{m_j} \right) \quad x = e^{-\beta(\epsilon_j - \mu)} \end{aligned}$$

For Fermions we get

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

thus, for Fermions

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

the thermodynamic potential (53) then becomes

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

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

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

and

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

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

$$\bar{m}_j = \langle m_j \rangle = \sum_{m_j} m_j P(m_j) = \sum_{m_j} m_j \frac{e^{-\beta(\epsilon_j - \mu)m_j}}{\Omega_j}$$

we may write this as

$$\langle \bar{m}_j \rangle = \frac{1}{\Omega_j} \left(- \frac{\partial}{\partial(\beta\epsilon_j)} \sum_{m_j} e^{-\beta(\epsilon_j - \mu)m_j} \right)$$

or

$$\langle \bar{m}_j \rangle = - \frac{\partial}{\partial(\beta\epsilon_j)} \ln \Omega_j$$

(58)

For Fermions Eq (54) gives

$$\begin{aligned} \langle \bar{m}_j \rangle &= - \frac{\partial}{\partial(\beta\epsilon_j)} \ln (1 + e^{-\beta(\epsilon_j - \mu)}) \\ &= \frac{e^{-\beta(\epsilon_j - \mu)}}{1 + e^{-\beta(\epsilon_j - \mu)}} \end{aligned}$$

or

$$\boxed{\langle \bar{m}_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}}$$

(Fermions)

(59)

This is called the Fermi-Dirac distribution.

For Bosons Eq (56) gives mean value of number of particles

$$\begin{aligned}\bar{m}_j &= -\frac{\partial}{\partial(\beta \epsilon_j)} \ln \left[\frac{1}{1 - e^{-\beta(\epsilon_j - \mu)}} \right] \\ &= \frac{\partial}{\partial(\beta \epsilon_j)} \ln (1 - e^{-\beta(\epsilon_j - \mu)}) \\ &= \frac{e^{-\beta(\epsilon_j - \mu)}}{1 - e^{-\beta(\epsilon_j - \mu)}}\end{aligned}$$

thus we get

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

(60)

This is called the Bose-Einstein distribution

Summary of useful formulas

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

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

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

Bosons

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

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

Fermions

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

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

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

abundance of species to present

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

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

$$\bar{n}_j = \frac{1}{e^{\beta(\epsilon_j - \mu)} \mp 1} \quad (62)$$

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

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

In this case (62) becomes

$$\bar{n}_j \simeq \frac{1}{e^{\beta(\epsilon_j - \mu)}} = e^{-\beta(\epsilon_j - \mu)} \quad (64)$$

For (61) we may use the Taylor expansion

$$\ln(1 \pm x) \simeq \pm x \quad (65)$$

We then get

Final Results are

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

or

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

Now let's try to understand what these results mean.

First, we use Eq (42) to compute

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

We then see that

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

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

$$\frac{\bar{n}_j}{N} \approx \frac{e^{-\beta\epsilon_j}}{\sum_j e^{-\beta\epsilon_j}} \quad (68)$$

This is the Maxwell-Boltzmann distribution. We may interpret \bar{n}_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 indistinguishability 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

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

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

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

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