Lecture 13: Quantum Distributions

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Description of Microstates in QM

- In Quantum Mechanics we deal with discrete (or quasi-discrete) energy levels:
  
  ![Energy Level Diagram](image)

- Let us concentrate on *quantum ideal gases*, i.e. ensembles of non-interacting quantum particles. In this case it is convenient to consider energy level diagrams for *one-particle* states.

- We can build a *many-particle* eigenstates of the system by populating different *one-particle* states.

- The *microstate* (i.e. snapshot) $n$ of an $N$-particle system can be described as a set of the population numbers $\{n_1, n_2, \ldots, n_k, \ldots, n_N\}$ corresponding to the states with energies $\{\epsilon_1, \epsilon_2, \ldots, \epsilon_k, \ldots, \epsilon_N\}$. 
Description of Microstates in Quantum Mechanics

- The energy of the microstate $n$ reads:

$$E_{n,N} = \sum_k \epsilon_k n_k,$$  \hspace{1cm} (1)

where the population numbers $n_k$ satisfy a constraint:

$$N = \sum_k n_k,$$  \hspace{1cm} (2)

- The constraint (2) causes difficulties in using the canonical distribution similarly to the conservation of energy for the microcanonical distribution.

- It is very convenient to relax constraint (2) and introduce the *grand canonical* distribution with chemical potential $\mu$:

$$\rho_{n,N} = \frac{1}{\Xi} \exp \left[ -\frac{(E_n - \mu N)}{T} \right] = \frac{1}{\Xi} \exp \left[ -\beta (E_n - \mu N) \right],$$  \hspace{1cm} (3)
Grand Partition Function

where $\beta = 1/T$ and the *grand partition function* can be calculated from the normalization condition:

$$\sum_{n,N} \rho_{n,N} = 1$$  \hspace{1cm} (4)

Using Eqs. (1)-(3) we obtain:

$$\rho_{n,N} = \frac{1}{\Xi} \exp \left[ -\beta \sum_k (\epsilon_k - \mu)n_k \right] = \frac{1}{\Xi} \prod_k' \left\{ \exp \left[ -\beta (\epsilon_k - \mu) \right] \right\}^{n_k},$$  \hspace{1cm} (5)

where the sign ‘ means that $n_k$ are constrained by Eq. (2).
Fermions and Bosons

Since Eq. (4) contains all possible $N$ and all possible combinations $n = \{n_k\}$ the constraint (2) becomes irrelevant and the grand partition function can be expressed as an infinite product over one-particle states $k$:

$$\Xi = \sum_N \sum_n' \prod_k \{\exp \left[ -\beta (\epsilon_k - \mu) \right]\}^{n_k}$$

$$= \prod_k \left( \sum_n \{\exp \left[ -\beta (\epsilon_k - \mu) \right]\}^{n_k} \right)$$

(6)

Now we need to examine fundamental restrictions imposed on the numbers $n_k$ by quantum mechanics. According to QM there are two types of indistinguishable particles:

- Fermions, i.e. particles with half-integer spin $s = (\hbar/2)k$, where $k = 1, 3, 5, \ldots$
- Bosons, i.e. particles with integer spin $s = \hbar k$, where $k = 0, 1, 2, \ldots$
Fermi-Dirac Statistics

- For fermions the wave function is *antisymmetric* under the exchange of *any two* particle labels:

  \[ \Psi(x_1, x_2, \ldots, x_k, \ldots) = -\Psi(x_2, x_1, \ldots, x_k, \ldots) \]

- As a result of this asymmetry the wave function is zero if *any two* particles have the same labels. The *Pauli principle* applies: there can be no more than *one* particle in one state, i.e.

  \[ n_k = 0, 1 \]

- Let us use the *grand potential*:

  \[ \Omega = -T \ln \Xi = \sum_k \Omega_k, \]

  where

  \[ \Omega_k = -T \ln \sum_{n_k} \{\exp[-\beta(\epsilon_k - \mu)]\}^{n_k} \] (7)
Fermi-Dirac Statistics

- Substituting $n_k = 0, 1$ in Eq. (7) we obtain:

$$\Omega_k = -T \ln \left[ 1 + e^{\beta(\mu - \epsilon_k)} \right]$$

- As in general

$$d\Omega = -SdT - pdV - \bar{N}d\mu \Rightarrow \bar{N} = - \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V}$$

Therefore

$$\bar{N} = \sum_k \bar{n}_k,$$

where

$$\bar{n}_k = \frac{\partial \Omega_k}{\partial \mu} = \frac{1}{\exp \left[ (\epsilon_k - \mu)/T \right] + 1} \quad \text{Fermi-Dirac distribution}$$
Bose-Einstein Statistics

- For bosons the wave function is *symmetric* under the exchange of *any two* particle labels:
  \[ \Psi(x_1, x_2, \ldots, x_k, \ldots) = \Psi(x_2, x_1, \ldots, x_k, \ldots) \]

- The *Pauli principle* does not apply, i.e. \( n_k \) can assume any value:
  \[ n_k = 0, 1, 2, \ldots, \infty \]

- To calculate \( \Omega_k \) we have to sum up a geometric series:
  \[
  \Omega_k = -T \ln \sum_{n_k=0}^{\infty} \{\exp[-\beta(\epsilon_k - \mu)]\}^{n_k} = T \ln (1 - \exp[\beta(\mu - \epsilon_k)])
  \]

- Therefore
  \[
  \bar{n}_k = \frac{\partial \Omega_k}{\partial \mu} = \frac{1}{\exp[(\epsilon_k - \mu)/T] - 1} \quad \text{Bose-Einstein distribution}
  \]