Physics 415 - Lecture 28: Quantum Statistics

April 2, 2025

Summary

- Canonical Ensemble (CE): Fixed T, N, V. $P_r = e^{-\beta E_r}/Z$, $Z = \sum_r e^{-\beta E_r}$ ($\beta = 1/T$). $F = -T \ln Z$.
- Grand Canonical Ensemble (GCE): Fixed T, μ, V. $P_r = e^{-\beta(E_r - \mu N_r)}/\mathcal{Z}$, $\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)}$. $\Phi = -T \ln \mathcal{Z}$. Relation $\mathcal{Z} = \sum_N e^{\beta \mu N} Z_N$. Mean particle number $\overline{N} = -(\partial \Phi / \partial \mu)_{T,V}$.

Quantum Ideal Gases (Identical Particles)

Energy of a state is $E = n_1 \epsilon_1 + n_2 \epsilon_2 + \cdots = \sum_r n_r \epsilon_r$, where ϵ_r are single-particle energy levels and n_r are occupation numbers. The allowed occupation numbers depend on the particle statistics:

$$n_r = \begin{cases} 0, 1, 2, \ldots & \text{Bose-Einstein (BE) Statistics (Bosons)} \\ 0, 1 & \text{Fermi-Dirac (FD) Statistics (Fermions)} \end{cases}$$

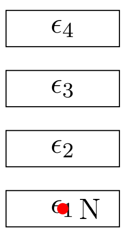
Total particle number constraint: $\sum_r n_r = N$.

Ground State (T=0)

Consider the drastic difference between BE and FD statistics in the quantum ground state (lowest total energy state). Let single-particle energies be ordered $\epsilon_1 < \epsilon_2 < \epsilon_3 < \ldots$.

BE Ground State: To minimize total energy $E = \sum n_r \epsilon_r$ subject to $\sum n_r = N$, all N particles occupy the lowest single-particle state ϵ_1.

- Occupation numbers: $n_r = N \delta_{r,1}$.
- Ground state energy: $E_{BE}^{(0)} = N \epsilon_1$.

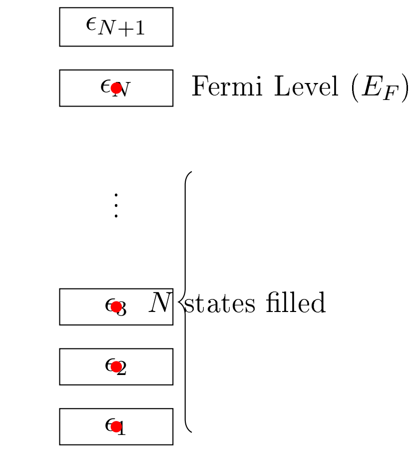


BE Ground State

FD Ground State: Due to the Pauli exclusion principle ($n_r = 0$ or 1), particles must fill the lowest available energy states, one particle per state, until all N particles are placed.

- Occupation numbers: $n_r = 1$ for $r = 1, \ldots, N$; $n_r = 0$ for $r > N$.
- Ground state energy: $E_{FD}^{(0)} = \epsilon_1 + \epsilon_2 + \cdots + \epsilon_N$.

Note that $E_{FD}^{(0)} > E_{BE}^{(0)}$ (for $N > 1$). The highest occupied energy level ϵ_N is called the Fermi energy E_F.



FD Ground State

Mean Occupation Numbers ($\overline{n}_r$)

When $T > 0$, particles will be "thermally excited" to higher energy states. This leads to a change in the mean occupation numbers $\overline{n}_r$. BE: $\overline{n}_1 < N$, $\overline{n}_{r>1} > 0$. FD: $\overline{n}_{r\leq N} < 1$, $\overline{n}_{r>N} > 0$.

Calculating $\overline{n}_r$ in the Canonical Ensemble (CE):

$$\overline{n}_r = \sum_{\{n_1,n_2,\dots\}}{}' P_{\{n_k\}} n_r$$

where $P_{\{n_k\}} = e^{-\beta \sum_k n_k \epsilon_k}/Z_N$ and the sum $\sum'$ is restricted by $\sum_k n_k = N$. It can be shown that:

$$\overline{n}_r = -\frac{1}{\beta}\frac{\partial(\ln Z_N)}{\partial \epsilon_r} = T\frac{\partial(\ln Z_N)}{\partial \epsilon_r}$$

(Similar to how $\overline{E} = -\partial(\ln Z)/\partial\beta$). However, calculating Z_N with the constraint $\sum n_r = N$ is challenging.

Using the Grand Canonical Ensemble (GCE)

The calculation becomes much simpler in the GCE because the constraint $\sum n_r = N$ is lifted (N fluctuates, fixed by reservoir μ). The sum over states $\{n_1, n_2, \dots\}$ becomes unrestricted (subject only to $n_r \geq 0$ for BE or $n_r \in \{0,1\}$ for FD). The grand partition function is:

$$\mathcal{Z} = \sum_{\{n_1,n_2,\dots\}} e^{-\beta \sum_k (\epsilon_k - \mu) n_k}$$

Because the sum in the exponent is over independent states k, and the sum over $\{n_k\}$ is unrestricted, the sum factorizes:

$$\mathcal{Z} = \left(\sum_{n_1} e^{-\beta(\epsilon_1-\mu)n_1}\right) \times \left(\sum_{n_2} e^{-\beta(\epsilon_2-\mu)n_2}\right) \times \cdots = \prod_r \left(\sum_{n_r} e^{-\beta(\epsilon_r-\mu)n_r}\right)$$

The sum $\sum_{n_r}$ depends on the statistics:

BE Statistics ($n_r = 0, 1, 2, \dots$): The sum is a geometric series: $\sum_{k=0}^{\infty} x^k = 1/(1-x)$, with $x = e^{-\beta(\epsilon_r-\mu)}$. The series converges only if $|x| < 1$, which requires $e^{-\beta(\epsilon_r-\mu)} < 1 \implies \epsilon_r - \mu > 0$, or $\mu < \epsilon_r$ for all r. Thus, the chemical potential μ must be less than the minimum single-particle energy ϵ_{min}.

$$\sum_{n_r=0}^{\infty} e^{-\beta(\epsilon_r-\mu)n_r} = \frac{1}{1-e^{-\beta(\epsilon_r-\mu)}}$$

$$\implies \mathcal{Z}_{BE} = \prod_r \frac{1}{1-e^{-\beta(\epsilon_r-\mu)}}$$

The grand potential $\Phi = -T\ln\mathcal{Z}$:

$$\Phi_{BE} = T\sum_r \ln(1-e^{-\beta(\epsilon_r-\mu)})$$

FD Statistics ($n_r = 0, 1$): The sum has only two terms:

$$\sum_{n_r=0}^{1} e^{-\beta(\epsilon_r-\mu)n_r} = e^0 + e^{-\beta(\epsilon_r-\mu)} = 1 + e^{-\beta(\epsilon_r-\mu)}$$

$$\implies \mathcal{Z}_{FD} = \prod_r (1+e^{-\beta(\epsilon_r-\mu)})$$

The grand potential:

$$\Phi_{FD} = -T\sum_r \ln(1+e^{-\beta(\epsilon_r-\mu)})$$

We can write a single expression for Φ covering both cases:

$$\Phi = \pm T\sum_r \ln(1\mp e^{-\beta(\epsilon_r-\mu)})$$

(Upper sign: BE, Lower sign: FD).

Mean Occupation Numbers $\overline{n}_r$ in GCE

The average occupation number of a single-particle state r is:

$$\overline{n}_r = \sum_{\{n_k\}} P_{\{n_k\}} n_r = \frac{1}{\mathcal{Z}} \sum_{\{n_k\}} n_r e^{-\beta\sum_k(\epsilon_k-\mu)n_k}$$

Because $\mathcal{Z}$ factorizes, $\mathcal{Z} = \mathcal{Z}_r \times \prod_{k\neq r}\mathcal{Z}_k$, where $\mathcal{Z}_r = \sum_{n_r} e^{-\beta(\epsilon_r-\mu)n_r}$. The average becomes:

$$\overline{n}_r = \frac{\sum_{n_r} n_r e^{-\beta(\epsilon_r-\mu)n_r}}{\sum_{n_r} e^{-\beta(\epsilon_r-\mu)n_r}}$$

(All terms from $k \neq r$ cancel between numerator and denominator). This average can be calculated using the logarithm trick:

$$\overline{n}_r = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_r}\ln\left(\sum_{n_r} e^{-\beta(\epsilon_r-\mu)n_r}\right)$$

BE Case: $\ln(\sum\dots) = -\ln(1-e^{-\beta(\epsilon_r-\mu)})$.

$$\overline{n}_r = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_r}[-\ln(1-e^{-\beta(\epsilon_r-\mu)})] = \frac{1}{\beta}\frac{1}{1-e^{-\beta(\dots)}}[-e^{-\beta(\dots)}(-\beta)]$$

$$\overline{n}_r = \frac{e^{-\beta(\epsilon_r-\mu)}}{1-e^{-\beta(\epsilon_r-\mu)}} = \frac{1}{e^{\beta(\epsilon_r-\mu)}-1}$$

This is the **Bose-Einstein distribution** function, giving the mean number of bosons in state r.

FD Case: $\ln(\sum \dots) = \ln(1 + e^{-\beta(\epsilon_r - \mu)})$.

$$\overline{n}_r = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_r}[\ln(1 + e^{-\beta(\epsilon_r-\mu)})] = -\frac{1}{\beta}\frac{1}{1+e^{-\beta(\dots)}}[e^{-\beta(\dots)}(-\beta)]$$

$$\overline{n}_r = \frac{e^{-\beta(\epsilon_r-\mu)}}{1+e^{-\beta(\epsilon_r-\mu)}} = \frac{1}{e^{\beta(\epsilon_r-\mu)}+1}$$

This is the **Fermi-Dirac distribution** function, giving the mean number of fermions in state r.

(Note: In both cases, $\overline{n}_r$ could also be obtained from $\overline{n}_r = -\partial\Phi/\partial\epsilon_r$, holding T, μ constant).

The mean total particle number is $\overline{N}$:

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

Let's check this yields $\sum_r \overline{n}_r$:

$$-\frac{\partial\Phi}{\partial\mu} = -\frac{\partial}{\partial\mu}\left[\pm T\sum_r \ln(1 \mp e^{-\beta(\epsilon_r-\mu)})\right]$$

$$= \mp T\sum_r \frac{1}{1\mp e^{-\beta(\dots)}}[\mp e^{-\beta(\dots)}(-\beta)(-\frac{\partial\mu}{\partial\mu})]$$

$$= \mp T\sum_r \frac{\mp\beta e^{-\beta(\epsilon_r-\mu)}}{1\mp e^{-\beta(\epsilon_r-\mu)}} = T\beta\sum_r \frac{e^{-\beta(\epsilon_r-\mu)}}{1\mp e^{-\beta(\epsilon_r-\mu)}}$$

$$= \sum_r \frac{1}{e^{\beta(\epsilon_r-\mu)}\mp 1} = \sum_r \overline{n}_r$$

So $\overline{N} = \sum_r \overline{n}_r$, an obvious result. If we view N as fixed, this equation becomes an implicit relation that determines $\mu = \mu(T, N, V)$.

Special Case: Photon Statistics

There are certain bosonic particles whose total number is not fixed (not conserved), e.g., photons (quantized oscillations of E&M field) which can be emitted and absorbed by atoms, or phonons/magnons (elementary excitations in solids). These are treated using Bose-Einstein statistics but without the constraint $\sum n_r = N$. This is equivalent to using the GCE formalism with chemical potential $\mu = 0$.

The mean occupation number becomes (Planck distribution):

$$\overline{n}_r = \frac{1}{e^{\beta\epsilon_r}-1}$$

Alternatively, calculate Z in CE but with unrestricted sum over $\{n_r\}$: $Z = \sum_{\{n_1,n_2,\dots\}} e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\dots)}$. Factorizes: $Z = (\sum_{n_1=0}^{\infty} e^{-\beta\epsilon_1 n_1})(\sum_{n_2=0}^{\infty} e^{-\beta\epsilon_2 n_2})\cdots = \prod_r \frac{1}{1-e^{-\beta\epsilon_r}}$. This matches $\mathcal{Z}_{BE}$ with $\mu = 0$.