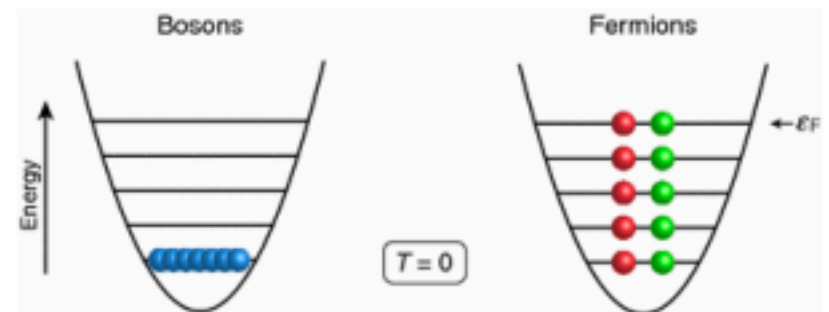


Lecture 29. *Bose-Einstein and Fermi-Dirac distributions*

- In this lecture, we will dig deeper into the importance of **quantum mechanics** and its effect on the statistical properties of gases
- We will consider how the fact particles are indistinguishable and their **wavefunctions** are constrained to adopt a certain symmetry has a profound impact on properties
- We will look at **bosons** and **fermions**



- **Fermion:** electrons, neutron, proton, ^3He (all spin 1/2); ^7He (spin 3/2)
- **Boson:** photons (spin 1)

Quantum description: a primer

- A quantum state is an abstract object that provides all the information of a quantum system. We call it, in Dirac notation, a *ket*
- The difficulty is of course to determine it
- We can determine the state using the Hamiltonian operator
- The wavefunction is a special representation of this object, yielding a somewhat more intuitive object like a function of space
- The physical interpretation is in the probability of finding the particle between x and $x + dx$
- The probability *amplitude* is a complex number

$$|\psi\rangle$$

Exchange and Symmetry

- Two particles: one at r_1 and one at r_2
- The wavefunction of this system is $\psi(r_1, r_2)$, so that $|\psi(r_1, r_2)|^2 dr_1 dr_2$ is a joint probability
- The Hamiltonian of the system *commutes* with the exchange operator $[\hat{\mathcal{H}}, \hat{P}_{12}] = 0$
 - \rightarrow the eigenfunctions of the two operators can be chosen to be the same
 - \rightarrow Because the two particles are the same
$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2$$
 - \rightarrow The two wave functions are chosen up to a phase factor

Exchange operator \hat{P}_{12}

$$\hat{P}_{12}\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1)$$

$$\hat{P}_{12}\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1) = \lambda\psi(\mathbf{r}_1, \mathbf{r}_2)$$

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \pm \psi(\mathbf{r}_1, \mathbf{r}_2)$$

- **Only two types of wavefunctions:**

- **Symmetric (+) “Bosons”** $\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)$
- **Anti-symmetric (-) “Fermions”** $\psi(\mathbf{r}_2, \mathbf{r}_1) = -\psi(\mathbf{r}_1, \mathbf{r}_2)$
 - Two fermions can't occupy the same position!

A wavefunction is a special representation of quantum states

- Imagine we have a particle in state 0 and another in state 1, we can describe the combined state as: $|0\rangle|1\rangle$

(1) Distinguishable particles: $|0\rangle|0\rangle, |1\rangle|0\rangle, |0\rangle|1\rangle, |1\rangle|1\rangle.$

(2) Indistinguishable and classical particles: $|0\rangle|0\rangle, |1\rangle|0\rangle, |1\rangle|1\rangle$

(3) Indistinguishable and quantum (bosons): $|0\rangle|0\rangle, |1\rangle|1\rangle, \frac{1}{\sqrt{2}}(|1\rangle|0\rangle + |0\rangle|1\rangle)$

(4) Indistinguishable and quantum (fermions): $\frac{1}{\sqrt{2}}(|1\rangle|0\rangle - |0\rangle|1\rangle)$

Note: for fermions, they cannot occupy the same quantum state! (Pauli exclusion principle)

Statistics of identical particles

- What happens when we have *many* identical particles (instead of just 2 as in the previous slide)?
- We have developed the tools: grand partition function! (**constraint:** number of particles is not fixed but the chemical potential is)

$$\mathcal{Z} = \sum_{\alpha} e^{\beta(\mu N_{\alpha} - E_{\alpha})}$$

Sum over all possible states of the system

Limiting case: just one state available

- Since the number of particles can change

$$\mathcal{Z} = \sum_n e^{n\beta(\mu-E)}$$

- For Fermions: we only have $n = 0$ or $n = 1$ (Pauli exclusion principle) $\mathcal{Z} = \sum_{n=0}^1 e^{n\beta(\mu-E)} = 1 + e^{\beta(\mu-E)} \rightarrow \ln \mathcal{Z} = \ln(1 + e^{\beta(\mu-E)})$

- For Bosons: any occupation number is possible $\mathcal{Z} = \sum_{n=0}^{\infty} e^{n\beta(\mu-E)} = \frac{1}{1 - e^{\beta(\mu-E)}} \rightarrow \ln \mathcal{Z} = -\ln(1 - e^{\beta(\mu-E)})$

We can condense:

$$\ln \mathcal{Z} = \pm \ln(1 \pm e^{\beta(\mu-E)})$$

$$\sum_{n=0}^{\infty} (r)^n = \frac{1}{1-r}$$

Limiting case: just one state available

Average number of particles

$$\mathcal{Z} = \sum_n e^{n\beta(\mu-E)} \quad \rightarrow \quad \langle n \rangle = \frac{\sum_n n e^{n\beta(\mu-E)}}{\sum_n e^{n\beta(\mu-E)}} = -\frac{1}{\beta \mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial E} = -\frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial E}$$

$$\ln \mathcal{Z} = \pm \ln(1 \pm e^{\beta(\mu-E)})$$



$$\langle n \rangle = \frac{1}{e^{\beta(E-\mu)} \pm 1}$$

Fermions (+)


Bosons (-)

General case

- Cost of putting a particle in i^{th} state: E_i
- Occupation number n_i (number of particles in state i)
- A configuration of the system is thus: $\left[e^{\beta(\mu - E_1)} \right]^{n_1} \times \left[e^{\beta(\mu - E_2)} \right]^{n_2} \times \dots = \prod_i e^{n_i \beta(\mu - E_i)}$

- The grand partition function is the sum of those products $\mathcal{Z} = \sum_{\{n_i\}} \prod_i e^{n_i \beta(\mu - E_i)}$

- If we only accept two cases: $n_i = 0$ or 1 (fermions) and $n_i = 0, 1, 2, 3, \dots$ (bosons), so n_i is independent of i :

$$\mathcal{Z} = \prod_i \sum_{\{n_i\}} e^{n_i \beta(\mu - E_i)}$$


$$\mathcal{Z} = \prod_i \sum_{\{n_i\}} e^{n_i \beta(\mu - E_i)}$$

$$\mathcal{Z} = \sum_{\{n_i\}} \prod_i e^{n_i \beta(\mu - E_i)}$$

$$\mathcal{Z} = (1 + e^{-\epsilon_1} + e^{-2\epsilon_1} + \dots)(1 + e^{-\epsilon_2} + e^{-2\epsilon_2} + \dots)(1 + e^{-\epsilon_3} + e^{-2\epsilon_3} + \dots) \dots$$

$$= \dots + e^{-2\epsilon_1} + e^{-2\epsilon_2} + e^{-2\epsilon_3} + e^{-(\epsilon_1 + \epsilon_2)} + e^{-(\epsilon_1 + \epsilon_3)} + e^{-(\epsilon_2 + \epsilon_3)} + \dots$$

$$\mathcal{Z} = (1 + e^{-\varepsilon_1}) (1 + e^{-\varepsilon_2}) (1 + e^{-\varepsilon_3}) \dots$$

Sum of all possible products!

(Fermionic case)

$$\mathcal{Z} = \prod_i \sum_{\{n_i\}} e^{n_i \beta (\mu - E_i)}$$

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

$$\mathcal{Z} = \prod_i \sum_{\{n_i\}} e^{n_i \beta (\mu - E_i)}$$

Fermions: $\mathcal{Z} = \prod_i (1 + e^{\beta(\mu - E_i)}) \longrightarrow \ln \mathcal{Z} = \sum_i \ln(1 + e^{\beta(\mu - E_i)})$

Bosons: $\mathcal{Z} = \prod_i (1 + e^{\beta(\mu - E_i)} + e^{2\beta(\mu - E_i)} + \dots) \longrightarrow \mathcal{Z} = \prod_i \frac{1}{1 - e^{\beta(\mu - E_i)}}$
 $\longrightarrow \ln \mathcal{Z} = - \sum_i \ln(1 - e^{\beta(\mu - E_i)})$

$$\ln \mathcal{Z} = \pm \sum_i \ln(1 \pm e^{\beta(\mu - E_i)})$$

Number of particles in each states

$$\ln \mathcal{Z} = \pm \sum_i \ln(1 \pm e^{\beta(\mu - E_i)})$$

$$\langle n_i \rangle = -\frac{1}{\beta} \left(\frac{\partial \ln \mathcal{Z}}{\partial E_i} \right) = \frac{e^{\beta(\mu - E_i)}}{1 \pm e^{\beta(\mu - E_i)}}$$

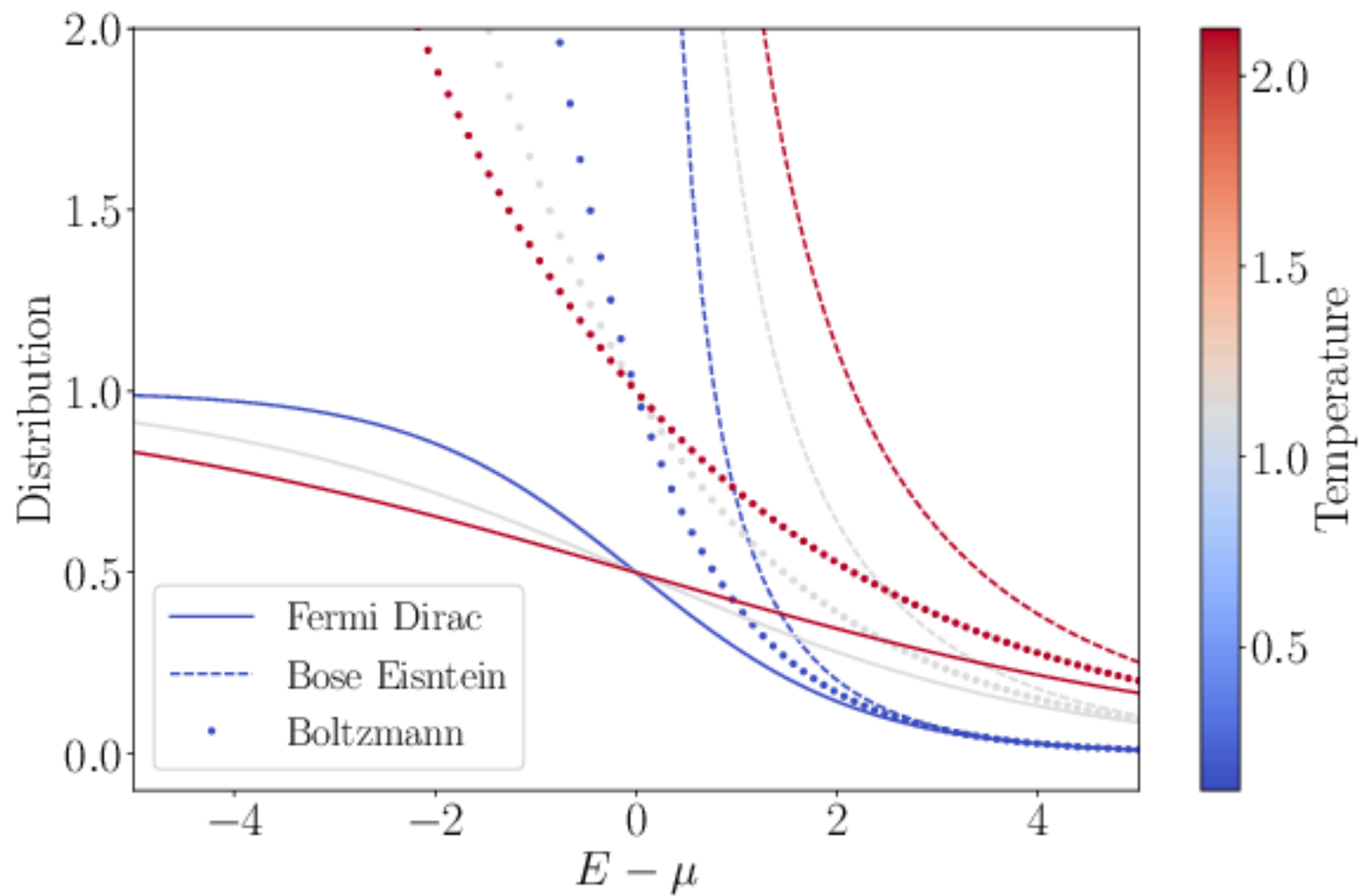
Grand Potential
(lecture 22)

$$\Phi_G = -k_B T \ln \mathcal{Z}$$

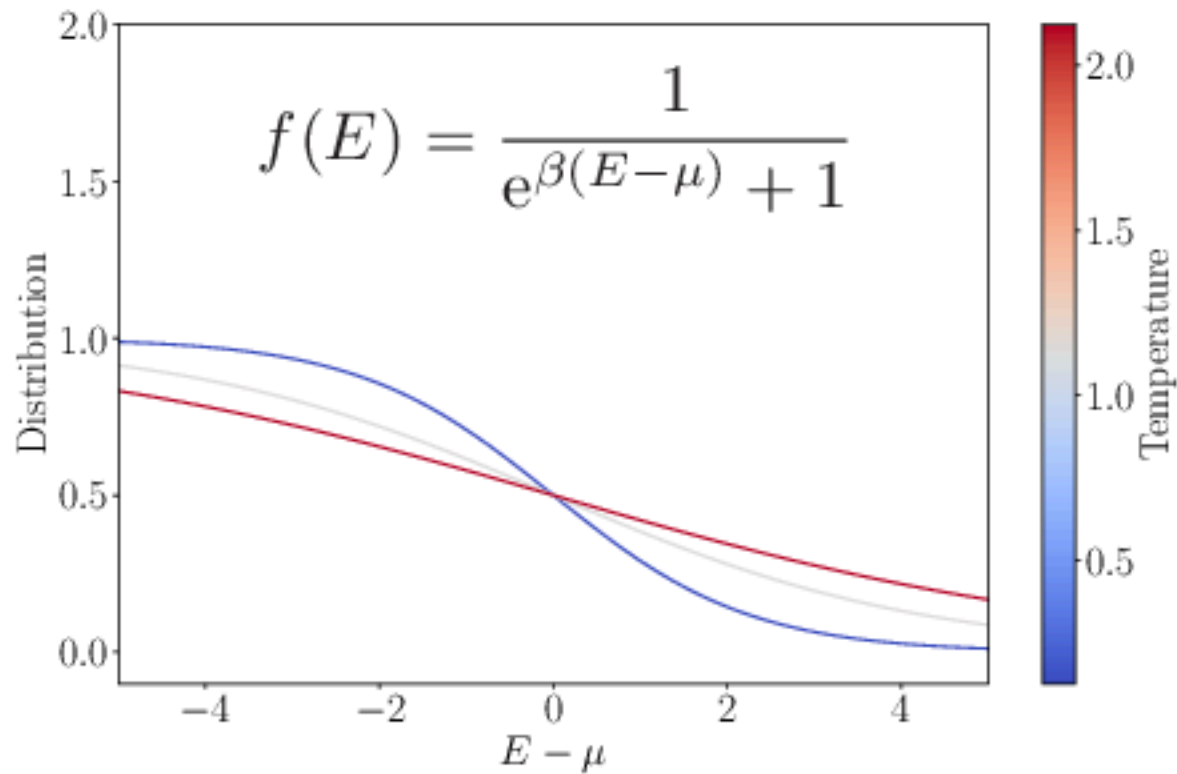
$$n_i = \left(\frac{\partial \Phi_G}{\partial E_i} \right)_{T,V}$$

Distribution functions: mean occupation of a state with energy E

- Fermi-Dirac distribution $f(E) = \frac{1}{e^{\beta(E-\mu)} + 1}$
- Bose-Einstein distribution $f(E) = \frac{1}{e^{\beta(E-\mu)} - 1}$

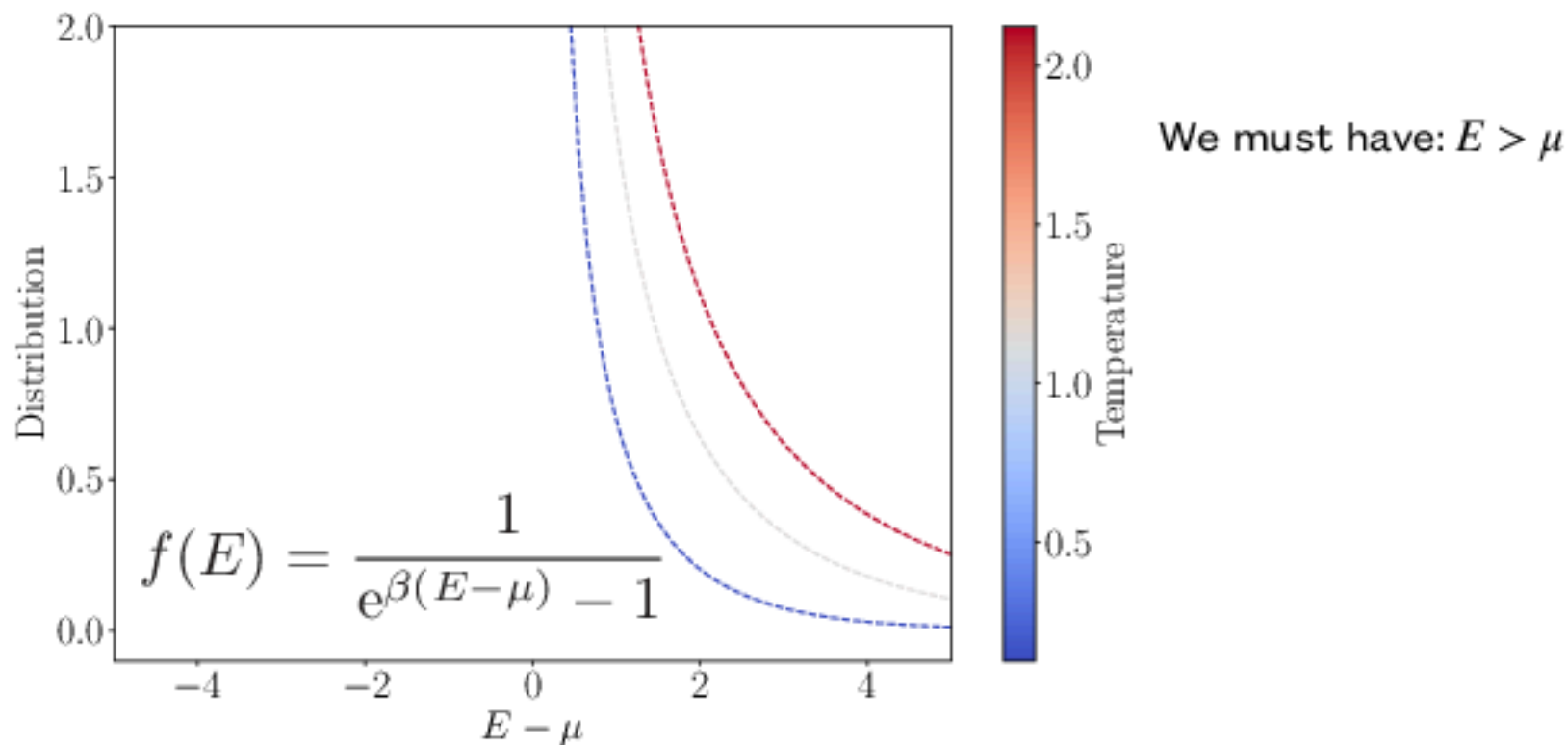


Fermi-Dirac

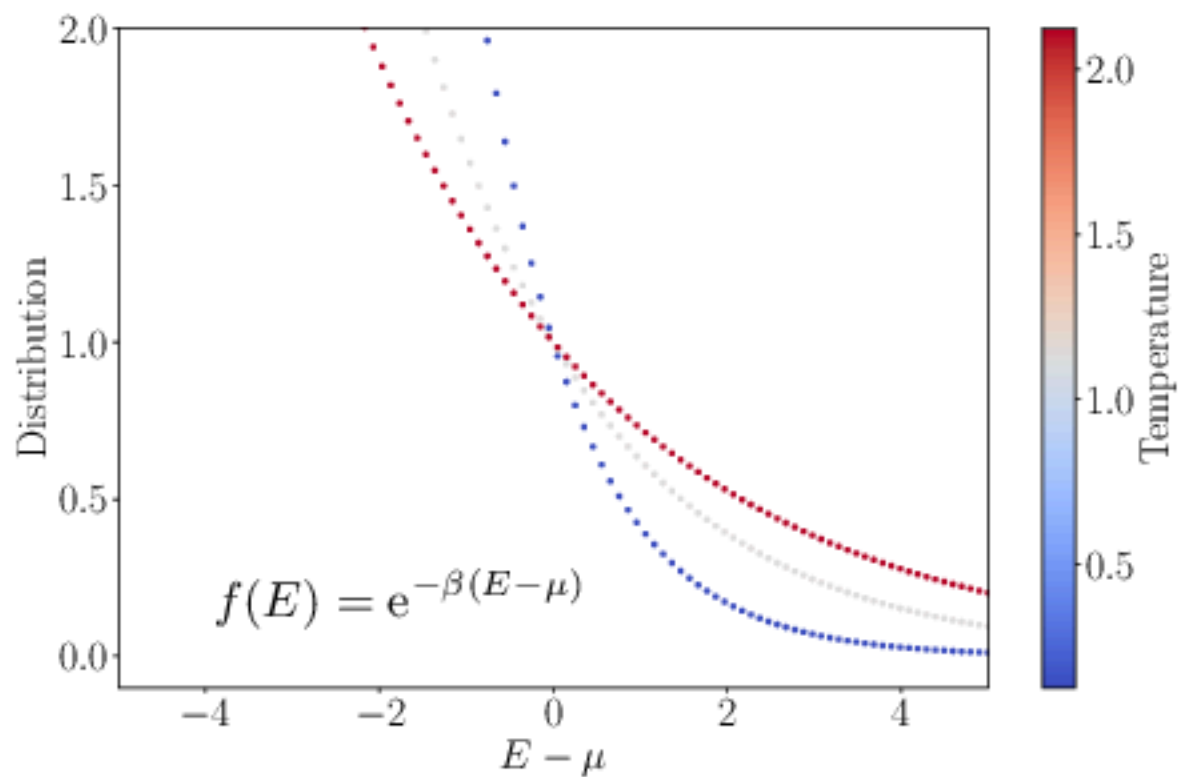


Pauli Principle

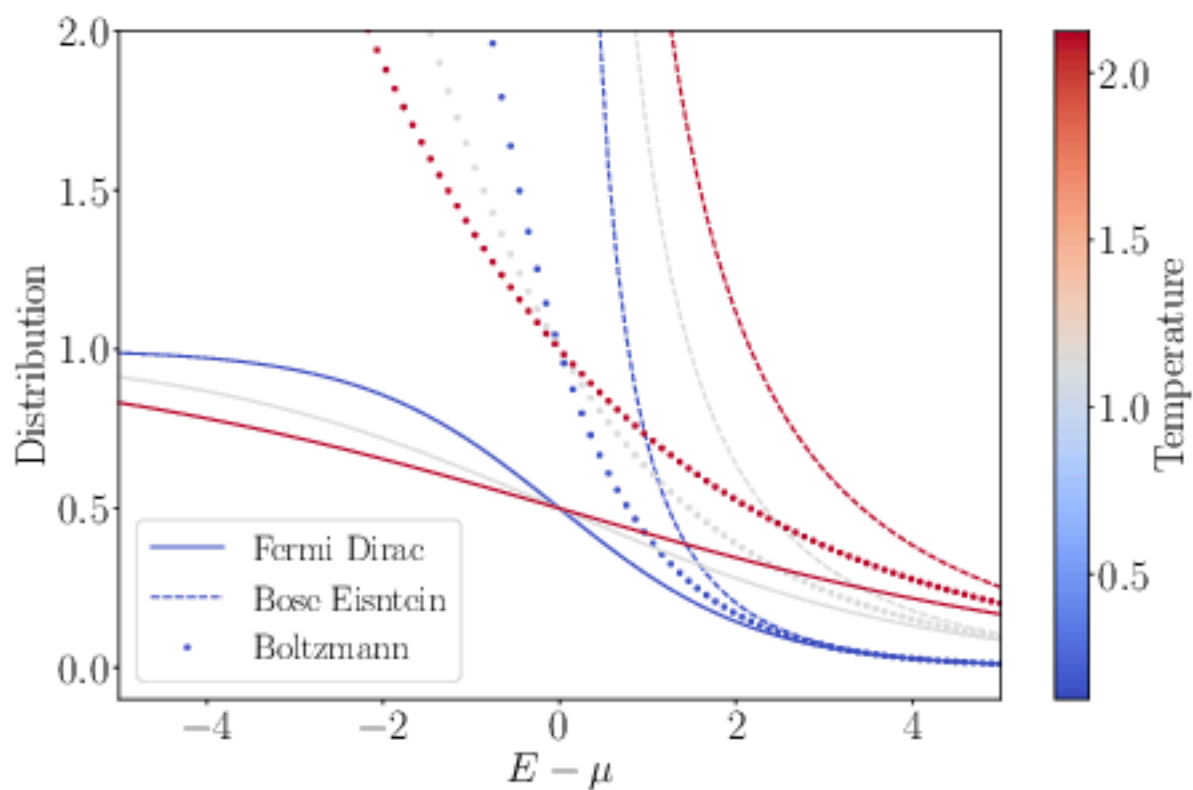
Bose-Einstein



Boltzmann



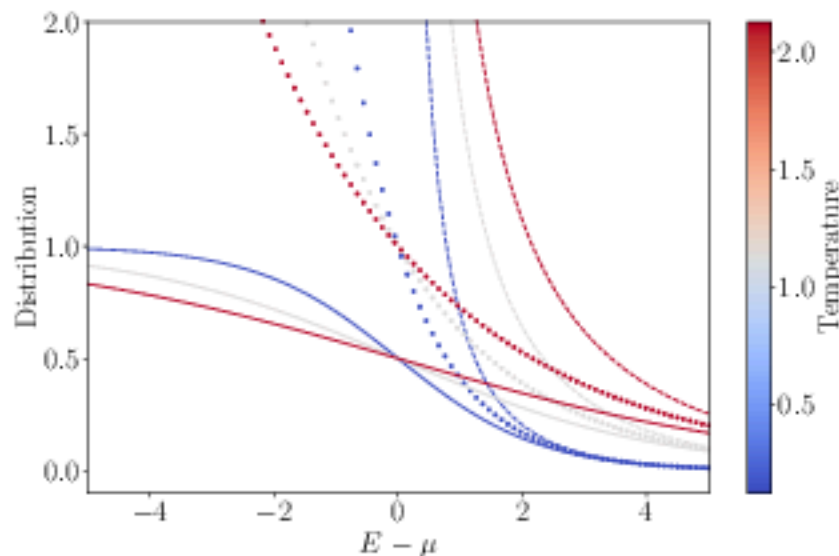
Comparing



Small chemical potential Limit

The chemical potential increases with the density n of particles: Particles flow from systems with high n to systems with low n .

$$\mu = k_B T \ln(n \lambda_{\text{th}}^3) \quad \text{Ideal gas}$$



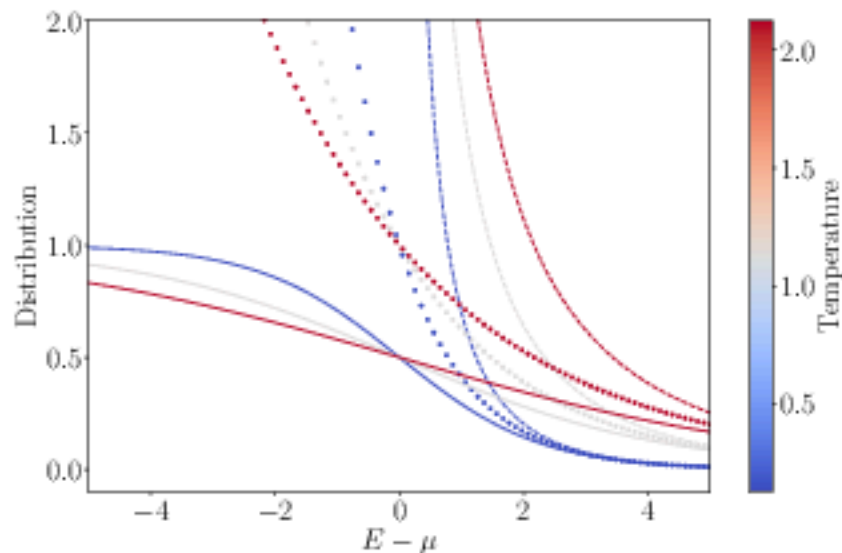
At high $E - \mu$, functions tend to the Boltzmann distribution because this limit corresponds to low density (small μ)

There are many more states thermally accessible to the particles than there are particles

Double occupancy never occurs and the requirements of exchange symmetry are inconsequential

Fermions and bosons behave like classical particles

High-density



The differences between the distributions are substantial at high density.

The distribution function for bosons diverges when $\mu = E$. Thus for bosons, the chemical potential must always be below the lowest-energy state. (Otherwise the lowest-energy state would become occupied with an infinite number of particles).

The implications for the properties of quantum gases will be considered in the next chapter.

Summary

The wave function of a pair of bosons is symmetric under exchange of particles, while the wave function of a pair of fermions is antisymmetric under exchange of particles.

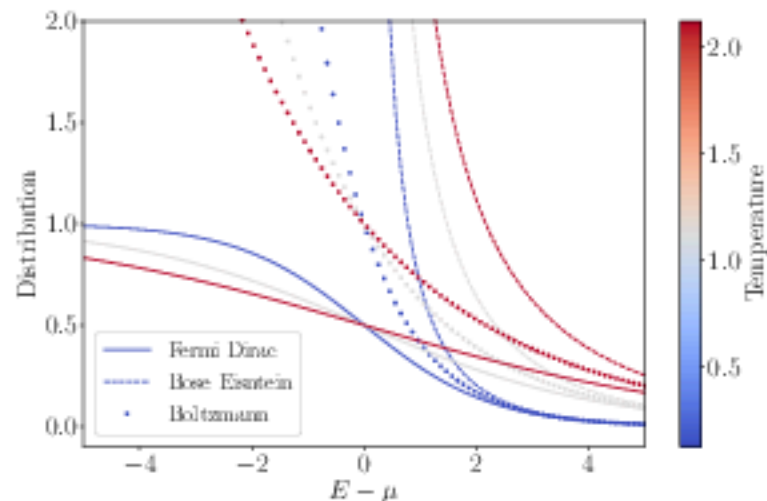
Bosons can share quantum states, while fermions cannot share quantum states.

Bosons obey Bose-Einstein statistics, given by

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

Fermions obey Fermi-Dirac statistics, given by

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



6.3. Critical Points

Take another look at Figure 6-2. There is an arrow at the top of the solid-liquid coexistence curve to indicate it goes on forever. No matter how high you make the pressure, there will always be two distinct phases and a transition between them. But the liquid-gas transition is another matter. The coexistence curve only goes so far, then comes to an end. The point at which it ends is called a *critical point*. Beyond that point, there are no longer separate liquid and gas phases, just a single phase called a *supercritical fluid*.

To understand why this happens, consider how the liquid and gas phases change as you increase the pressure. The liquid phase is difficult to compress, so pressure changes have little effect on it. The gas phase, on the other hand, is very compressible. As you increase the pressure, its volume decreases steadily. That, of course, means that its entropy decreases too: less volume means fewer possible positions for each molecule. At the same time, its energy also decreases. As the molecules are forced closer together, it becomes easier for them to form hydrogen bonds, so the average number of hydrogen bonds steadily increases.

The upshot is that as you increase the pressure, the free energy difference between the two phases decreases. Eventually it reaches zero, and there is no longer any free energy difference at all. That is what happens at the critical point.

To be clear, it is not just that there is no longer a free energy difference. *There is no longer any difference at all between the phases.* The essential difference between the solid and liquid can be described by two numbers: the average distance between molecules, and the average number of hydrogen bonds per molecule. In the liquid phase the molecules stay close to each other, held together by hydrogen bonds. In the gas phase, they spread out to fill all available volume. But what if they have no extra volume to fill? If the pressure is high enough, the system no longer has any ability to increase its entropy by spreading out. In that case, there is no longer any distinction between the two phases. That happens at the critical point. Beyond it, there is no longer a phase transition, just a single phase.

Why does the solid-liquid coexistence curve go on forever, while the liquid-gas curve ends at a critical point? What is different about these two transitions to produce such different behavior? The answer, it turns out, is a matter of symmetry.

In physics, a symmetry of a system is a way you can transform the system that leaves it unchanged. Think of a square, for example. If you rotate it by 90 degrees around its center, it is unchanged. The same is true if you rotate it by 180 or 270 degrees. In each case, the rotation maps the square back onto itself, so you are left with an identical square. You also can mirror the square about a horizontal, vertical, or diagonal line passing through its center. Each of these is a symmetry of the square. The set of all symmetries of a system is called its *symmetry group*.

The liquid and gas phases of water have no symmetries. They consist of molecules arranged at random, not following any regular pattern, so there is no transformation that leaves them unchanged. The solid phase, on the other hand, does have symmetries. For example, if you translate the entire crystal by exactly one lattice spacing, that maps the lattice back onto itself. There are also ways you can rotate or mirror the crystal that leave it unchanged.

The solid phase always has these symmetries, independent of pressure and temperature. There is no point in the phase diagram at which it does not have them. Likewise, there is no point in the phase diagram at which the liquid phase does have these symmetries. That is why the change from one to the other must always involve an abrupt transition in which the symmetry is formed or destroyed. In contrast, since the liquid and gas phases have identical symmetry groups, you can follow a path through the phase diagram that continuously changes one into the other.

This idea is called the *Landau symmetry principle*. It states that if two phases have different symmetry groups, they must always be separated by a phase transition. No matter what path you take between them, there must be some point at which the system abruptly changes from one phase to the other.