

## Outline Notes: Lectures 9-14

# Indistinguishable Particles

## 6 Gases (Lecture 9)

Consider a gas of identical particles. The particles are indistinguishable. Rather than being localized at individual sites, the particles share a common volume and occupy a shared set of single-particle states. This will change how we count microstates for the system: microstates will be described in terms of occupancies of the shared single-particle states. First we need to calculate the single-particle states.

### 6.1 Density of states

The Schrödinger equation for a non-relativistic particle in free space (zero potential) is

$$\frac{-\hbar^2}{2m} \nabla^2 \psi = \epsilon \psi.$$

This has the travelling wave solutions

$$\psi = A e^{i\mathbf{k} \cdot \mathbf{r}}$$

with energy given by the dispersion relationship

$$\epsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m},$$

where  $k^2 = |\mathbf{k}|^2$ .

We need to be able to count the number of states available to the particle as a function of energy. (By states we mean orthogonal single-particle states.) Since in free space the energy is directly related to the momentum, we shall consider the momentum states. Consider first a cubic region of space  $V = L^3$ . Supposing we start with a travelling wave state with a wavefunction  $A e^{i\mathbf{k}_0 \cdot \mathbf{r}}$  then we can generate a complete set of wavefunctions that are orthogonal over the volume  $V$  by adding to  $\mathbf{k}_0$  a wavevector

$$\mathbf{k} = (k_x, k_y, k_z) = \left( \frac{2\pi l}{L}, \frac{2\pi m}{L}, \frac{2\pi n}{L} \right) \quad \text{for any integers } l, m \text{ and } n.$$

These orthogonal states are uniformly spaced in  $\mathbf{k}$ -space with a  $\mathbf{k}$ -space volume of  $(2\pi/L)^3$  per state. The density of states in  $\mathbf{k}$ -space is then

$$\left( \frac{L}{2\pi} \right)^3 = \frac{V}{(2\pi)^3}.$$

Note that this does not depend on any boundary conditions our region might have. Boundary conditions may constrain the phase of the wavefunction (i.e., the complex values of the coefficient  $A$ ) and the choice of  $\mathbf{k}_0$ . They will not change the spacing of the orthogonal states.

The number of states in an elemental volume of  $\mathbf{k}$ -space,  $d^3k = dk_x dk_y dk_z$  is

$$dg = V \frac{d^3k}{(2\pi)^3} = V \frac{d^3p}{h^3}$$

where  $d^3p = dp_x dp_y dp_z$  is the corresponding element of momentum space ( $\mathbf{p} = \hbar\mathbf{k}$ .) So far we have found the density of states in momentum or  $\mathbf{k}$ -space. We can integrate to get the number of states with wavenumber  $k$  to  $k + dk$ ,

$$dg = g(k) dk = V \frac{1}{(2\pi)^3} 4\pi k^2 dk = \frac{1}{2\pi^2} V k^2 dk$$

$$\Rightarrow g(k) = \frac{1}{2\pi^2} V k^2.$$

$g(k)$  is the density of states in wavenumber.

We can now calculate the corresponding density of states in energy. If we define  $g(\epsilon)$  to be the density of states in energy, then the number of states with energies between  $\epsilon$  and  $\epsilon + d\epsilon$  corresponding to wavenumbers  $k$  to  $k + dk$  is

$$dg = g(\epsilon)d\epsilon = g(k)dk \quad \Rightarrow \quad g(\epsilon) = g(k) \frac{dk}{d\epsilon}.$$

Using the dispersion relationship,

$$k = \frac{\sqrt{2m\epsilon}}{\hbar}, \quad \frac{d\epsilon}{dk} = \frac{\hbar^2 k}{m} = \hbar \sqrt{\frac{2\epsilon}{m}}.$$

So the density of states in energy is

$$\begin{aligned} g(\epsilon) &= \frac{1}{2\pi^2} V \frac{2m\epsilon}{\hbar^2} \times \frac{1}{\hbar} \sqrt{\frac{m}{2\epsilon}} \\ &= \frac{V}{2\pi^2 \hbar^3} 2^{1/2} m^{3/2} \epsilon^{1/2} \\ &= \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2}. \end{aligned}$$

This is the density of states in energy for a non-relativistic free particle. Using the density of states, a summation over individual states can be replaced with an integration over the density of states. This approach will be valid provided the states are closely spaced in energy.

Note:

- The number of states between  $\epsilon$  and  $\epsilon + d\epsilon$  is proportional to the volume. Although we have used a cubic region of space, for simplicity, the result does not depend significantly on this choice. For example, we could consider a more complex volume as comprised of several cubic regions, and sum their component densities of states.
- The density of states does not depend on the boundary conditions or the choice of wavefunction basis. We could have chosen to use standing waves and we would have obtained the same result.

- This is just the density of states for translational motion. Particles may have internal states, e.g., spin states. If there is no energy associated with the internal states, that will give a degeneracy, i.e., for each translation state there will be several distinct single-particle states corresponding to the different internal states. We will represent this as a degeneracy factor  $D$ , the number of single-particle states per translation state.

## 7 Classical ideal gas

### 7.1 The Boltzmann distribution for a classical ideal gas

Consider a dilute ideal gas. By ideal we mean no interaction between the particles of the gas. We can therefore assume that the single-particle states are valid. We shall start from the canonical ensemble for a single particle.

#### 7.1.1 From the canonical ensemble

Consider a single molecule of gas in a container which is at temperature  $T$ . The molecule can be treated as a system in a heat bath. The microstates are the single-particle states and so the probability that the molecule is in the  $j$ th single-particle state, which has energy  $\epsilon_j$ , is given by the canonical ensemble,

$$p_j = \frac{1}{Z} e^{-\epsilon_j/k_B T} \quad \text{where} \quad Z = \sum_j e^{-\epsilon_j/k_B T}.$$

$Z$  is the partition function for a single particle — the sum is over the single-particle states. For  $N$  particles, provided  $p_j N \ll 1$ , we can neglect multiple occupancies of states.<sup>1</sup> Then each molecule can be treated as a system in a heat bath provided by the rest of the molecules. The average number of particles in the  $j$ th single-particle state is the *mean occupancy* of the state,

$$f_j = N p_j = \frac{N}{Z} e^{-\epsilon_j/k_B T}$$

where  $Z$  is the single-particle partition function. This is the Boltzmann distribution for a classical gas. It is only valid for  $f_j \ll 1$ .

#### 7.1.2 Alternative derivation: from the microcanonical ensemble (\*OPTIONAL\*)

We cannot simply follow the approach we took for the system of distinguishable particles to find the equilibrium configuration. Since the microstates are defined by the occupancies of the states, we would find that each configuration corresponds to just one microstate. For the maximum entropy approach to work, a configuration needs to have a sufficiently large number of microstates that it can be representative of the system as a whole. One possible solution is to bundle the single-particle states together into groups (see e.g., Dugdale or Guénault). Here we present an approach that considers a large assembly of identical systems and defines configurations for the whole assembly.

Imagine an assembly comprising a large number  $N_A$  of identical systems with average energy  $U$  and average number of particles  $N$ . The assembly is isolated. For example, we could envisage the assembly as consisting of small cubic regions in a much larger volume of a gas, each cubic region representing one system. Each system has an identical set of single-particle states  $\psi_j$  with energies  $\epsilon_j$ . The particles are free to move between the different states.

Consider the  $j$ th single-particle state from every system in the assembly. Summing across the whole assembly, this state contains  $n_j$  particles. The set of  $n_j$  defines a configuration for the assembly  $\mathbf{n} = [n_0, n_1, \dots]$ . We want to find the equilibrium configuration, i.e., the most

<sup>1</sup>This will prove to be a key assumption for a classical gas.

likely. For the  $j$ th single-particle state, the number of ways of arranging the  $n_j$  indistinguishable particles between the  $N_A$  systems is

$$\frac{N_A^{n_j}}{n_j!}$$

provided  $n_j \ll N_A$ . This is the multiplicity associated with the  $j$ th single-particle state across the assembly. The statistical weight for the configuration is the product of the multiplicities for each single-particle state,

$$\Omega_n = \prod_j \frac{N_A^{n_j}}{n_j!} \quad \Rightarrow \quad \ln \Omega_n = \sum_j n_j \ln(N_A/n_j) + n_j \quad (\text{using Stirling}).$$

To find the equilibrium configuration we maximize  $\ln \Omega_n$  subject to the constraints, which are

$$\sum_j n_j = N_A N, \quad \sum_j n_j \epsilon_j = N_A U.$$

Using the Lagrange method of undetermined multipliers as before,

$$\frac{\partial}{\partial n_j} \left[ \ln \Omega_n - \alpha \sum_j n_j - \beta \sum_j \epsilon_j n_j \right] = 0 \quad \text{for all } j.$$

This gives

$$\ln(N_A/n_j) - \alpha - \beta \epsilon_j = 0 \quad \text{for all } j.$$

$$\Rightarrow \quad \frac{n_j}{N_A} = e^{-\alpha - \beta \epsilon_j}$$

As before,  $\beta = 1/k_B T$  and  $e^{-\alpha}$  is a normalization constant (for the number of particles).

Then for one system, the average number of particles in the  $j$ th single particle state, i.e., the *mean occupancy* of the state, is

$$f_j = \frac{n_j}{N_A} = \frac{N}{Z} e^{-\epsilon_j/k_B T}$$

where  $Z$  is again the single-particle partition function.

## 7.2 Partition function for an ideal gas (Lecture 10)

The partition function for a single particle is the sum over all states. However, the energy levels for the single-particle translation states are very closely spaced so we can replace the summation with an integral over the density of states,

$$Z = \int_0^\infty D g(\epsilon) e^{-\epsilon/k_B T} d\epsilon$$

where  $D$  is the degeneracy and  $g(\epsilon)$  is the density of states. Substituting the previously calculated density of states  $g(\epsilon)$  for a free particle,

$$Z = \int_0^\infty D \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} e^{-\epsilon/k_B T} d\epsilon.$$

Using a standard integral,

$$\int_0^\infty x^{1/2} e^{-ax} dx = \frac{\pi^{1/2}}{2a^{3/2}}$$

this gives for the partition function for a single particle,

$$Z = D V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2}.$$

## 7.3 Thermodynamics of an ideal classical gas

Now we have the partition function, we can proceed to calculate thermodynamic properties. For  $N$  independent identical molecules, the partition function factorizes as before. However, now we have indistinguishable particles we can no longer distinguish between different permutations of the particles, so we have to divide by the number of permutations  $N!$ . The  $N$  particle partition function is then

$$Z = \frac{Z_{(1)}^N}{N!}$$

where  $Z_{(1)}$  is the partition function for a single molecule. Warning: the factor  $N!$  is only correct for very dilute gases such that the probability of more than one particle in a state can be ignored. The factor makes no difference for some thermodynamic quantities, but is important for entropy.

The log of the partition function is then given by (using Stirling's approximation),

$$\begin{aligned} \ln Z &= N \ln Z_{(1)} - (N \ln N - N) \\ &= N (\ln Z_{(1)} - \ln N + 1) \\ &= N \left[ \ln D + \ln V + \frac{3}{2} \ln T - \ln N + \frac{3}{2} \ln \left( \frac{2\pi m k_B}{h^2} \right) + 1 \right]. \end{aligned}$$

The internal energy is then,

$$U = k_B T^2 \frac{\partial \ln Z}{\partial T} = \frac{3N k_B T}{2}.$$

This agrees with the thermodynamics result for a monatomic ideal gas ( $\frac{1}{2} k_B T$  per degree of freedom.)

The Helmholtz function is

$$F = -k_B T \ln Z$$

$$= -k_B T N \left[ \ln D + \ln V + \frac{3}{2} \ln T - \ln N + \frac{3}{2} \ln \left( \frac{2\pi m k_B}{h^2} \right) + 1 \right]$$

from which we can calculate the pressure,

$$P = - \left( \frac{\partial F}{\partial V} \right)_T = k_B T \left( \frac{\partial \ln Z}{\partial V} \right)_T = \frac{N k_B T}{V}.$$

This is the ideal gas law.

Calculating the entropy,

$$S = - \left( \frac{\partial F}{\partial T} \right)_V = k_B T \left( \frac{\partial \ln Z}{\partial T} \right)_V + k_B \ln Z$$

$$= N k_B \left[ \ln D + \ln V + \frac{3}{2} \ln T - \ln N + \frac{3}{2} \ln \left( \frac{2\pi m k_B}{h^2} \right) + \frac{5}{2} \right].$$

This is the Sackur–Tetrode equation for the entropy of a monatomic ideal gas.

## 7.4 Maxwell–Boltzmann speed distribution

Now we have the mean occupancy and the density of states, we can calculate further properties of the gas. The number of particles with speeds  $v$  to  $v + dv$  is given by

$$n(v) dv = D g(v) f(v) dv$$

where  $g(v)$  is the density of states in speed and  $f(v)$  is the mean occupancy of states with speed  $v$ . The number of states with speeds  $v$  to  $v + dv$ , corresponding to wavenumbers  $k$  to  $k + dk$  is

$$dg = g(v) dv = g(k) dk, \quad \Rightarrow \quad g(v) = g(k) \frac{dk}{dv}.$$

But,  $v = p/m = \hbar k/m$  and using the previously derived density of states in wavenumber gives

$$g(v) = g(k) \frac{dk}{dv} = V \frac{k^2}{2\pi^2} \frac{m}{\hbar} = V \frac{m^3 v^2}{2\pi^2 \hbar^3} = 4\pi V \frac{m^3}{h^3} v^2.$$

The mean occupancy is

$$f(\epsilon) = \frac{N}{Z_1} e^{-\epsilon/k_B T}$$

$$\Rightarrow f(v) = \frac{N}{Z_1} e^{-mv^2/2k_B T}$$

$$= \frac{N}{DV} \left( \frac{h^2}{2\pi m k_B T} \right)^{3/2} e^{-mv^2/2k_B T}.$$

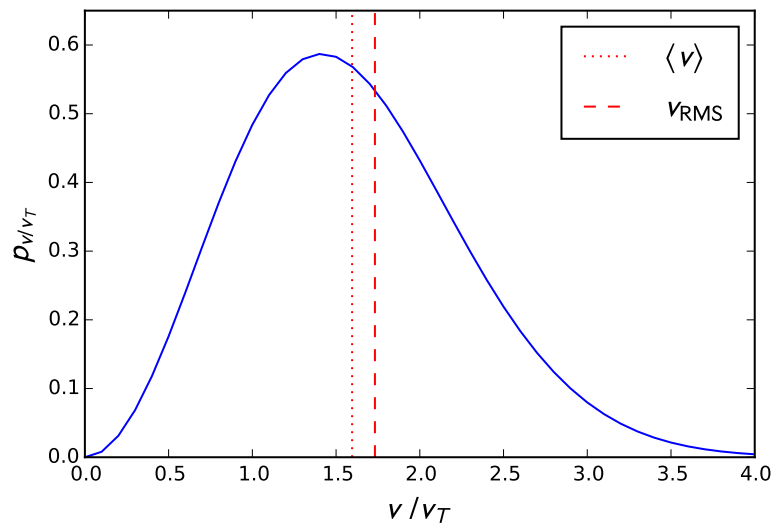


Figure 1: Maxwell–Boltzmann speed distribution ( $v_T = \sqrt{k_B T/m}$ )

Therefore

$$\begin{aligned}
 n(v) dv &= D 4\pi V \frac{m^3}{h^3} v^2 \frac{N}{DV} \left( \frac{h^2}{2\pi m k_B T} \right)^{3/2} e^{-mv^2/2k_B T} dv \\
 &= N \sqrt{\frac{2}{\pi}} \left( \frac{m}{k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} dv.
 \end{aligned}$$

This is the Maxwell–Boltzmann speed distribution. Note that this result is purely classical — there is no Planck constant. The result was first derived classically by Maxwell.

It is useful to define a thermal speed,

$$v_T = \sqrt{\frac{k_B T}{m}}$$

Then three characteristic speeds are:

- The most probable speed,  $v_{\text{MAX}} = \sqrt{2}v_T$ ,
- The mean speed,  $\langle v \rangle = \sqrt{8/\pi}v_T$ ,
- the RMS speed,  $v_{\text{RMS}} = \sqrt{\langle v^2 \rangle} = \sqrt{3}v_T$ .

The RMS speed is related to the kinetic energy. The mean kinetic energy is

$$\text{mean KE} = \frac{1}{2} m v_{\text{RMS}}^2 = \frac{3}{2} k_B T,$$

again in agreement with equipartition.

In terms of the thermal speed, with  $v' = v/v_T$ , the Maxwell–Boltzmann speed distribution is

$$n(v') dv' = N \sqrt{\frac{2}{\pi}} v'^2 e^{-v'^2/2} dv'.$$



## 8 Quantum statistics: fermions and bosons (Lecture 11)

**Fermions** Particles with half-integer spin.

Wavefunctions are antisymmetric with respect to exchange of the particle labels giving a maximum occupancy of one for a single-particle state (Pauli exclusion principle).

Examples: electron, proton, neutron,  $^3\text{He}$ , quark, neutrino.

**Bosons** Particles with integer spin.

Wavefunctions are symmetric with respect to exchange of particle labels, so there is no limit on the occupancy of a single-particle state.

Examples: photon, W, Z, Higgs, phonon,  $^4\text{He}$ .

### 8.1 Equilibrium distributions

Consider a system of indistinguishable identical particles. The system has a set of single-particle states that are shared by the particles. The fundamental indistinguishability of quantum particles means that specifying the occupancy for each of the single-particle states completely specifies a microstate of the system.

There are a large number of these single-particle states in the system and particles can move between them. We can therefore treat each single-particle state as a distinct system that has its own set of microstates corresponding to the possible values of its occupancy. The single-particle states are weakly interacting in that particles can move between them, but the energies of their microstates do not depend on the occupancies of the other single-particle states.

The system corresponding to the  $j^{\text{th}}$  single-particle state will have a set of microstates corresponding to the possible values of its occupancy  $n_j$ . The microstates have energies  $n_j\epsilon_j$ , where  $\epsilon_j$  is the energy of one particle in the single-particle state. The grand partition function for the  $j^{\text{th}}$  single-particle-state system is then

$$\mathcal{Z}_j = \sum_{n_j} e^{-(n_j\epsilon_j - n_j\mu)\beta} = \sum_{n_j} e^{n_j(\mu - \epsilon_j)\beta},$$

where the summation is over the possible values of the occupancy  $n_j$ . The probability that there are  $n_j$  particles in the  $j^{\text{th}}$  single-particle state is then

$$p(n_j) = \frac{1}{\mathcal{Z}_j} e^{n_j(\mu - \epsilon_j)\beta}.$$

The expectation (the mean occupancy) of the state in equilibrium is then given by

$$\langle n_j \rangle = \sum_{n_j} n_j p(n_j) = \frac{1}{\mathcal{Z}_j} \frac{\partial \mathcal{Z}_j}{\partial (\mu\beta)}.$$

### 8.2 Fermions

For fermions, the possible values of the occupancy are 0 or 1. Thus the grand partition function is

$$\mathcal{Z}_j = \sum_{n_j=0}^1 e^{n_j(\mu - \epsilon_j)\beta} = 1 + e^{(\mu - \epsilon_j)\beta}.$$

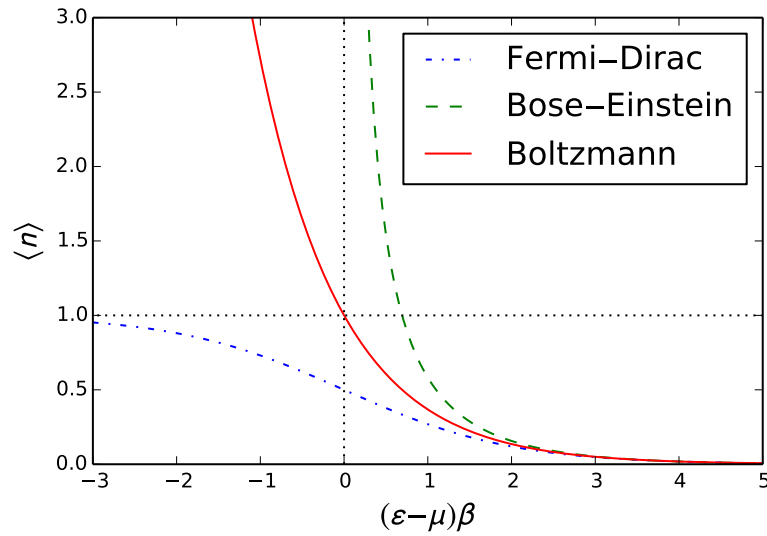


Figure 2: Fermi-Dirac, Bose-Einstein and Boltzmann distributions

Then the mean occupancy of the  $j^{\text{th}}$  state is

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

Since this only depends on the energy level of the single-particle state, and using  $\beta = 1/k_B T$ , we write the mean occupancy for fermions as

$$f_{\text{FD}} = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1},$$

which is the Fermi-Dirac distribution.

### 8.3 Bosons

For bosons, the Pauli exclusion principle does not apply and so the grand partition function is

$$\mathcal{Z}_j = \sum_{n_j=0}^{\infty} e^{n_j(\mu - \epsilon_j)\beta} = \frac{1}{1 - e^{(\mu - \epsilon_j)\beta}},$$

[where we have used the standard result  $\sum_{n=0}^{\infty} x^n = 1/(1 - x)$ ].

The mean occupancy is then

$$\langle n_j \rangle = \frac{e^{(\mu - \epsilon_j)\beta}}{1 - e^{(\mu - \epsilon_j)\beta}} = \frac{1}{e^{(\epsilon_j - \mu)\beta} - 1},$$

which gives for the Bose-Einstein distribution

$$f_{\text{BE}} = \frac{1}{e^{(\epsilon - \mu)/k_B T} - 1}.$$

## 8.4 Summary

Writing the classical Boltzmann distribution in the same form for comparison we have

$$f = \frac{1}{e^{(\epsilon - \mu)/k_B T} \pm 1} \quad \begin{cases} +1 & \text{Fermi-Dirac} \\ -1 & \text{Bose-Einstein} \end{cases}$$

$$f = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 0} \quad \begin{cases} +0 & \text{Boltzmann (classical — dilute only!)} \end{cases}$$

Note:

- Both Fermi-Dirac and Bose-Einstein distributions approximate to the Boltzmann distribution in the dilute limit,  $(\epsilon - \mu)/k_B T \gg 1$ ,
- For the Bose-Einstein distribution,  $\mu < \epsilon$ .
- For the Fermi-Dirac distribution,  $\langle n \rangle \approx 1$  for  $(\epsilon - \mu) \ll k_B T$ .

## 9 Photon gas (Lecture 12)

For bosons, the Bose–Einstein distribution is

$$f_{\text{BE}} = \frac{1}{e^{(\epsilon - \mu)/k_{\text{B}}T} - 1},$$

where  $\mu \leq \epsilon$  for all states to ensure  $f_{\text{BE}}$  is finite.

### 9.1 Cavity (black-body) radiation

Consider a cavity of volume  $V$  with internal walls at fixed temperature  $T$ . The radiation inside the cavity is in thermal contact with the walls of the cavity — radiation can be absorbed, reflected and emitted at the walls. The radiation will therefore be in thermal equilibrium at temperature  $T$  so we can use the Bose–Einstein distribution to describe it. For a photon gas, the number of particles is not conserved. Therefore the chemical potential,  $\mu = 0$ .<sup>2</sup> Then, for photons,

$$f_{\text{BE}} = \frac{1}{e^{\epsilon/k_{\text{B}}T} - 1} = \frac{1}{e^{\hbar\omega/k_{\text{B}}T} - 1}$$

The number of photons with (angular) frequency  $\omega$  to  $\omega + d\omega$  is given by

$$n(\omega) d\omega = D g(\omega) f_{\text{BE}}(\omega) d\omega,$$

where  $g(\omega)$  is the density of states in  $\omega$  and  $D$  is the degeneracy factor.

#### 9.1.1 Density of states for photons

The wave equation for E-M waves in free space is

$$\nabla^2 \mathbf{E} = \frac{1}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} \quad \text{with solutions} \quad \mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)},$$

which gives the energy dispersion relationship

$$\omega = kc.$$

The number of states with wavenumber  $k$  to  $k + dk$  is given by the density of states in wavenumber,

$$dg = g(k) dk = \frac{V}{2\pi^2} k^2 dk.$$

Using the dispersion relationship allows us to derive the density of states in  $\omega$ , thus

$$\begin{aligned} g(\omega) &= g(k) \frac{dk}{d\omega} = \frac{V}{2\pi^2} k^2 \times \frac{1}{c} \\ \Rightarrow dg &= g(\omega) d\omega = \frac{V}{2\pi^2 c^3} \omega^2 d\omega. \end{aligned}$$

<sup>2</sup>Equivalently, we can think of this as not having the original constraint on number of particles in the Lagrangian that gave rise to the chemical potential in the first place.

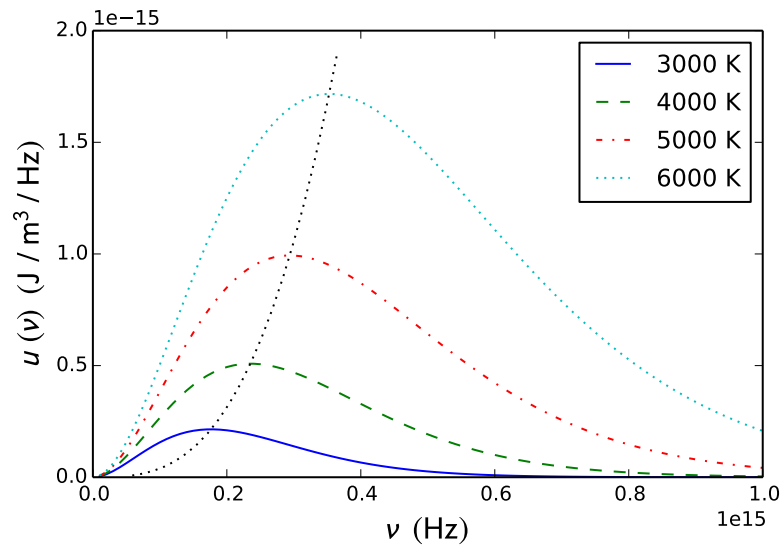


Figure 3: Planck black-body radiation law. Also plotted is the peak energy density.

### 9.1.2 Planck radiation law

For each travelling wave mode there are two independent polarizations, and so the degeneracy factor is  $D = 2$ . This then gives for the number of photons,

$$\begin{aligned} n(\omega) d\omega &= 2 \times \frac{V}{2\pi^2 c^3} \omega^2 \times \frac{1}{e^{\hbar\omega/k_B T} - 1} d\omega \\ &= \frac{V}{\pi^2 c^3} \frac{\omega^2}{e^{\hbar\omega/k_B T} - 1} d\omega. \end{aligned}$$

The spectral energy density,  $u(\omega)$  is then given by

$$\begin{aligned} u(\omega) d\omega &= \hbar\omega \frac{n(\omega)}{V} d\omega \\ &= \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1} d\omega. \end{aligned}$$

This is the Planck radiation law. In terms of frequency  $\nu = \omega/2\pi$ , the spectral energy density is given by

$$u(\nu) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_B T} - 1} d\nu.$$

Note that the energy density increases with temperature.

The peak of the spectrum depends on temperature,

$$\nu_{\text{MAX}} \approx 2.82 \frac{k_B T}{h}.$$

This is Wien's displacement law.

## 9.2 Stefan–Boltzmann law

If we integrate the spectral energy density, we obtain the total energy density,

$$\begin{aligned}
 U &= \int_0^\infty u(\nu) d\nu \\
 &= \frac{8\pi h}{c^3} \left( \frac{k_B T}{h} \right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx \\
 &= \frac{8\pi^5 h}{15c^3} \left( \frac{k_B T}{h} \right)^4
 \end{aligned}$$

(using the substitution  $x = h\nu/k_B T$  to transform the integral into a standard form integral, and then using the value for which being  $\pi^4/15$ .)

$U$  is the total energy density. From this we can calculate the radiation flux. For isotropic radiation, the radiance in any direction (i.e., the radiation power per unit solid angle crossing a unit surface normal to the direction) is given by

$$L = \frac{1}{4\pi} U c.$$

Then, if the cavity has a small entrance (small enough so that the radiation entering and leaving does not alter the thermal equilibrium of the radiation in the cavity), the radiation flux leaving the cavity entrance is

$$j^* = 2\pi \frac{L}{2} = \frac{Uc}{4}.$$

Substituting for the energy density this gives

$$j^* = \sigma T^4, \quad \text{where} \quad \sigma = \frac{2\pi^5 k_B^4}{15h^3 c^2} \approx 5.67 \times 10^{-8} \text{ Js}^{-1} \text{ m}^{-2} \text{ K}^{-4}.$$

This is the Stefan–Boltzmann law for the emissivity of a black body i.e., the energy flux leaving a black body.

## 10 Bose–Einstein condensation (Lecture 13)

Consider a system comprising a fixed number of non-relativistic bosons with mass  $m$  in thermal equilibrium at temperature  $T$ . The occupancy of the  $j^{\text{th}}$  state with energy  $\epsilon_j$  is given by the Bose–Einstein distribution,

$$f_{\text{BE}}(\epsilon_j) = \frac{1}{e^{(\epsilon_j - \mu)/k_B T} - 1}.$$

The occupancies of the states must sum to the total number of particles,

$$N = \sum_j f_{\text{BE}}(\epsilon_j).$$

Assuming that the states are closely spaced, we replace the summation with an integral over the density of states,

$$N = \int_0^\infty f_{\text{BE}}(\epsilon) g(\epsilon) d\epsilon,$$

(where for simplicity we have assumed a degeneracy factor of 1). Recall that the density of states for a non-relativistic particle is

$$g(\epsilon) = \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2},$$

giving

$$\begin{aligned} N &= \int_0^\infty \frac{1}{e^{(\epsilon - \mu)/k_B T} - 1} \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon \\ &= \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{e^{(\epsilon - \mu)/k_B T} - 1} d\epsilon. \end{aligned}$$

The total number of particles in the system is a function of both the chemical potential and the temperature. Therefore, when the number of particles is fixed, changing the temperature will cause the chemical potential to adjust such that the sum over the occupancies of the states remains constant. However, to ensure finite occupancy in every state, the chemical potential must also satisfy  $\mu < \epsilon_0$ , where  $\epsilon_0$  is the ground state energy, which we take to be zero. Setting  $\mu = 0$  in the above integral over the density of states gives

$$\begin{aligned} N_{\mu=0} &= \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{e^{\epsilon/k_B T} - 1} d\epsilon \\ &= 2\pi V \left( \frac{2mk_B T}{h^2} \right)^{3/2} \int_0^\infty \frac{x^{1/2}}{e^x - 1} dx \\ &= \zeta\left(\frac{3}{2}\right) V \left( \frac{2\pi mk_B T}{h^2} \right)^{3/2}, \end{aligned}$$

where we have used the result of a standard integral,

$$\int_0^\infty \frac{x^{1/2}}{e^x - 1} dx = \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right),$$

and where the Riemann zeta function has value  $\zeta(\frac{3}{2}) \approx 2.61$ . Since setting  $\mu = 0$  corresponds to the maximum value of this integral, this would appear to indicate that  $N_{\mu=0}$  is the maximum number of particles that the system can contain for a given temperature  $T$ . Equivalently, it suggests that for a given number of particles  $N$ , there is a minimum temperature below which the system cannot be cooled,

$$T > T_B = \frac{h^2}{2\pi m k_B} \left( \frac{N}{V \zeta(3/2)} \right)^{2/3}.$$

This would be strange.

In fact, there is a problem in our calculation. The approximation of the summation over the discrete energy states with the density of states integral is only valid if the integrand varies slowly compared with the spacing of the energy levels (i.e.,  $k_B T \gg \delta_\epsilon$ ). For low temperatures this condition is not satisfied at the lower end of the integration near  $\epsilon = 0$ . Up to now, this has not mattered since ordinarily the contribution from this region would have been negligible as the number of states affected is rather small. However, as we go to even lower temperatures the expected occupancy of those states becomes bigger and the error in neglecting them becomes more significant, with the consequence that at very low temperatures a significant contribution from the ground state is not properly accounted for. We therefore attempt to refine our approximation by including an extra term to account for the ground state contribution separately, so that the total number of particles is given by

$$N = n_0 + \int_0^\infty f_{BE}(\epsilon) g(\epsilon) d\epsilon,$$

where the occupancy of the ground state is

$$n_0 = \frac{1}{e^{-\mu/k_B T} - 1}.$$

and the integral accounts for the other states, the excited states. For temperatures  $T < T_B$  we expect the number of particles in the ground state to be large and so

$$n_0 = \frac{1}{e^{-\mu/k_B T} - 1} \approx -\frac{k_B T}{\mu} \quad \Rightarrow \quad -\mu \approx \frac{k_B T}{n_0}.$$

Thus,  $\mu$  is very close to zero and so for  $T < T_B$  we can use  $N_{\mu=0}$  for the density of states integral for number of particles in the excited states. The fraction of particles in these excited states is then

$$\frac{N - n_0}{N} \approx \frac{N_{\mu=0}(T)}{N} = \left( \frac{T}{T_B} \right)^{3/2}.$$

$T_B$  is the critical temperature, or the Bose temperature. Below this temperature, the number of particles in the ground state becomes macroscopically large. This is Bose–Einstein condensation.

We can express the critical temperature  $T_B$  in terms of an energy,  $k_B T_B$  or, since that energy is entirely kinetic energy, in terms of a momentum. Then the de Broglie wavelength corresponding to the critical temperature,  $\lambda_B$  is given by

$$p = \frac{h}{\lambda_B} = \sqrt{2m k_B T_B} \quad \Rightarrow \quad \lambda_B \approx 2.4 \left( \frac{V}{N} \right)^{1/3}.$$

Thus, at the critical temperature, the de Broglie wavelength of a particle with the typical thermal energy is longer than the particle spacing.



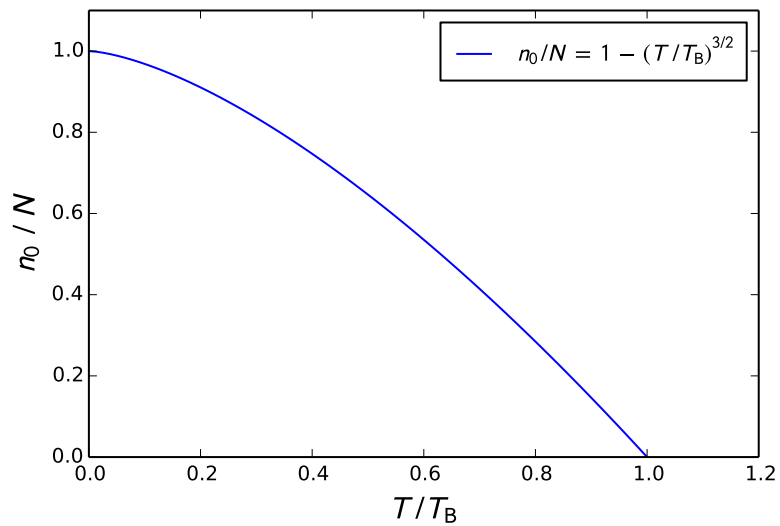


Figure 4: Fraction of particles in the ground state as a function of temperature for a macroscopic Bose–Einstein condensate.

## 11 Fermi gases (Lecture 14)

The Fermi–Dirac distribution for a system of identical fermions in thermal equilibrium is

$$f_{\text{FD}} = \frac{1}{e^{(\epsilon - \mu)/k_{\text{B}}T} + 1}.$$

### 11.1 The Fermi level

At low temperatures, there is a rapid transition between filled and unfilled states, the distribution becoming a step function as the temperature tends to zero,

$$\lim_{T \rightarrow 0} f_{\text{FD}} = \begin{cases} 1 & \text{if } \epsilon < \mu, \\ 0 & \text{if } \epsilon > \mu. \end{cases}$$

At  $T = 0$ , all states below  $\epsilon = \mu$  are filled, and all states above are empty. In this case we refer to the gas as being *degenerate*.<sup>3</sup> The chemical potential at  $T = 0$  defines the *Fermi energy*,

$$\epsilon_{\text{F}} = \mu|_{T=0}.$$

Note that the chemical potential itself depends on the temperature.

Since the Fermi level is the boundary between the filled ( $\epsilon < \epsilon_{\text{F}}$ ) and the empty ( $\epsilon > \epsilon_{\text{F}}$ ) states at  $T = 0$ , the total number of states up to the Fermi level must equal the number of particles in the system,

$$N = \int_0^{\epsilon_{\text{F}}} D g(\epsilon) d\epsilon.$$

So, for free, non-relativistic electrons, with a degeneracy factor of 2 due to their spin, the total number of electrons in a volume  $V$  satisfies

$$\begin{aligned} N &= \int_0^{\epsilon_{\text{F}}} 2 \frac{2\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon \\ &= \left( \frac{2m\epsilon_{\text{F}}}{h^2} \right)^{3/2} \frac{8\pi V}{3} \end{aligned}$$

from which we obtain the Fermi energy,

$$\epsilon_{\text{F}} = \frac{h^2}{2m} \left( \frac{3}{8\pi} \right)^{2/3} \left( \frac{N}{V} \right)^{2/3}.$$

It is also useful to define a corresponding temperature, the Fermi temperature as  $T_{\text{F}} = \epsilon_{\text{F}}/k_{\text{B}}$ . For  $T \gg T_{\text{F}}$ , the occupancy  $f_{\text{FD}}$  is very small for all energies and the gas approximates the classical Maxwell–Boltzmann. For  $T \sim T_{\text{F}}$ , this is no longer the case and quantum statistics are needed, and for  $T \ll T_{\text{F}}$  the degenerate situation is a very good approximation.

<sup>3</sup>not to be confused with the other meaning of degeneracy referring to multiple states for an energy level.

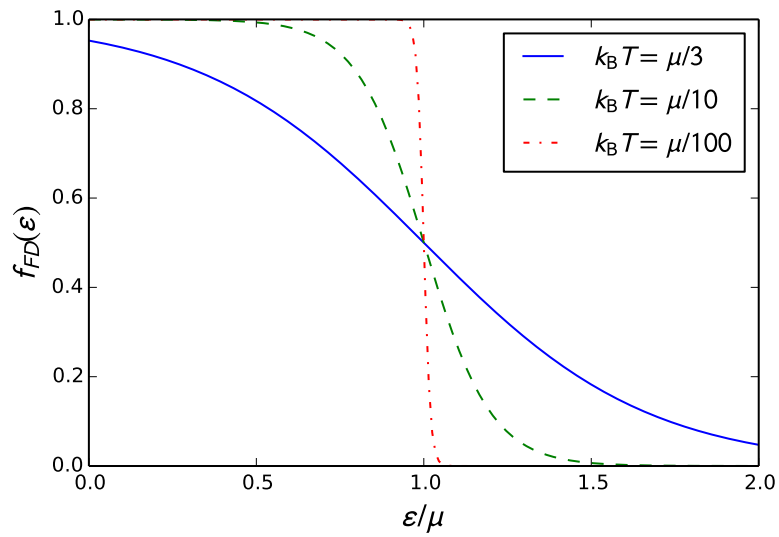


Figure 5: The Fermi–Dirac distribution for different values of temperature.

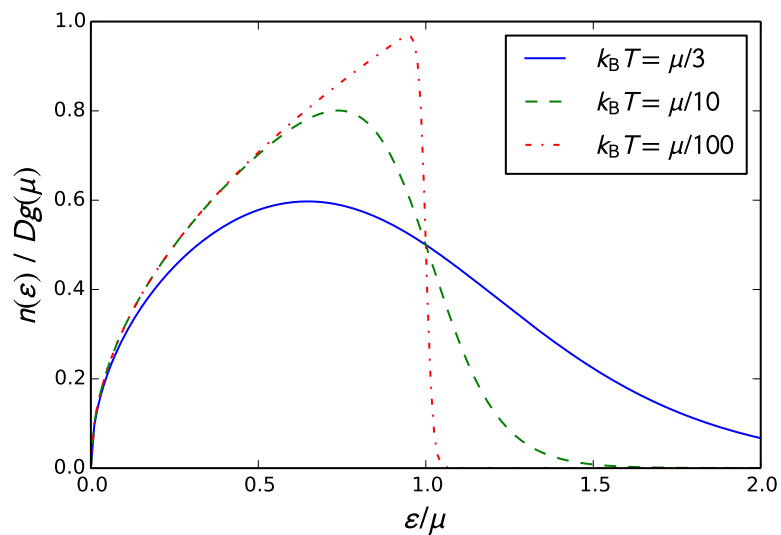


Figure 6: The energy distribution of particles for a free, non-relativistic Fermi gas for different values of temperature. (Note that the chemical potential itself varies with temperature.)

## 11.2 Thermodynamic properties of degenerate Fermi gases

The internal energy of the gas is given by

$$U = \int_0^\infty n(\epsilon) \epsilon d\epsilon$$

$$= \int_0^\infty D g(\epsilon) f_{FD}(\epsilon) \epsilon d\epsilon.$$

In the limit  $T \rightarrow 0$ , this becomes

$$U = \int_0^{\epsilon_F} D g(\epsilon) \epsilon d\epsilon.$$

Since the density of states varies as  $g(\epsilon) \propto \epsilon^{1/2}$  for a non-relativistic free particle, this gives

$$U = A \int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon = \frac{2A}{5} \epsilon_F^{5/2}.$$

Similarly, the total number of particles satisfies

$$N = A \int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon = \frac{2A}{3} \epsilon_F^{3/2},$$

from which we can calculate the total internal energy as

$$U = \frac{3}{5} N \epsilon_F.$$

Therefore, even at zero temperature, the degenerate Fermi gas can have significant internal energy. However, at  $T = 0$ , the entropy is zero.

We can also calculate the pressure of the degenerate gas. From the fundamental thermodynamic equation for a gas,

$$P = - \left( \frac{\partial U}{\partial V} \right)_S = - \frac{3}{5} N \left( \frac{\partial \epsilon_F}{\partial V} \right)_S = \frac{2}{5} \frac{N}{V} \epsilon_F.$$

Substituting the Fermi energy for free electrons gives

$$P = \frac{h^2}{5m} \left( \frac{3}{8\pi} \right)^{2/3} \left( \frac{N}{V} \right)^{5/3}.$$

It can be seen that the pressure increases non-linearly with the density. The Fermi gas has significant pressure at zero temperature. This is the *degeneracy pressure*.

## 11.3 Electrons in metal

In a metal the valence electrons are weakly bound and non-localized. To first approximation, we can consider the electrons as free particles in a smooth potential due to the positive ions and the other electrons. These electrons will therefore behave as a Fermi gas.

For example, for copper,

$$\text{density} = 8.96 \times 10^3 \text{ kg m}^{-3}, \quad \text{atomic mass} = 63.5 \text{ u}.$$

Each ion contributes one electron to the conduction band, so the number of electrons per unit volume is

$$\frac{N}{V} = 8.50 \times 10^{28} \text{ m}^{-3}.$$

Using the density of states for free electrons, this gives a Fermi energy and Fermi temperature

$$\epsilon_F = 7.05 \text{ eV}, \quad T_F = 8.18 \times 10^4 \text{ K}.$$

At room temperature,  $T \ll T_F$  and the valence electrons approximate well to a degenerate Fermi gas. The gas is not fully degenerate: the finite temperature means that near the Fermi level, some states below it are empty and some above are filled.

For an isotropic system, the Fermi energy corresponds to a sphere in  $\mathbf{k}$ -space. The surface corresponding to the Fermi energy in  $\mathbf{k}$ -space is called the *Fermi surface*. We can define the Fermi momentum and the Fermi speed as the momentum and speed of particles at the Fermi level,

$$p_F = \hbar k_F = \sqrt{2m\epsilon_F}, \quad v_F = \sqrt{2\epsilon_F/m}.$$

For copper, this gives the velocity of the electrons near the Fermi level as  $v_F \approx 1.6 \times 10^6 \text{ m/s}$ . In practice, the ionic lattice means that the dispersion is not isotropic, which affects the shape of the Fermi surface.

## 11.4 White dwarf stars

For stars in the main sequence (most observable stars), the primary source of energy is fusion of hydrogen to helium. In such stars the gravitational force is balanced by radiation pressure with energy supplied by the fusion process. The more massive the star, the higher the rate of fusion and the hotter and larger it is. However once the supply of hydrogen is exhausted, the star will begin to collapse under its own gravity. Eventually, the degeneracy pressure from the electrons in the star may be sufficient to balance the gravity. A white dwarf is such a star.

Consider a star of mass  $M$  and radius  $R$ . Assuming that the star is of uniform density, the gravitational potential energy is

$$U_G = -\frac{3}{5} \frac{GM^2}{R} = -C_1 \frac{M^2}{R}.$$

The internal energy of a uniform degenerate electron gas is

$$\begin{aligned} U_D &= \frac{3}{5} N \epsilon_F \\ &= \frac{3}{5} \left( \frac{h^2}{2m} \right) \left( \frac{3}{8\pi} \right)^{2/3} \frac{N^{5/3}}{V^{2/3}}. \end{aligned}$$

Substituting  $V = \frac{4}{3}\pi R^3$  for the volume and  $N = M/\mu_e$  for the number of electrons where  $\mu_e$  is the mass per electron gives

$$U_D = C_2 \frac{M^{5/3}}{R^2} \quad \text{where} \quad C_2 = \frac{9\sqrt[3]{12}h^2}{160\pi^{4/3}m_e\mu_e^{5/3}}.$$

The total potential energy is then

$$U = U_G + U_D = -C_1 \frac{M^2}{R} + C_2 \frac{M^{5/3}}{R^2}.$$

For the star to be stable  $U$  must be a minimum, so

$$\frac{dU}{dR} = 0 \quad \Rightarrow \quad R = \frac{2C_2}{C_1} M^{-1/3}.$$

For a star comprised of low-mass nuclei (He, C, etc) there are approximately equal numbers of neutrons and protons, giving approximately two nucleons per electron and  $\mu_e \approx 2m_p$ .

Substituting in values and expressing in terms of the standard solar mass  $M_\odot$  and radius  $R_\odot$ , this gives

$$R/R_\odot \approx 0.010(M/M_\odot)^{-1/3}.$$

This is the radius for which the electron degeneracy pressure balances the gravitational force. Note that the stable radius varies inversely with the mass. The corresponding density is

$$\rho \approx 1.3 \times 10^9 (M/M_\odot)^2 \text{ kg/m}^3.$$

The Fermi energy is

$$\epsilon_F \approx 0.19(M/M_\odot)^{4/3} \text{ MeV}.$$

Note that a full treatment involves solving the hydrostatic equilibrium equation and accounting for relativistic effects in the dispersion. This leads to an upper limit on the mass for which the star is stable, the Chandrasekhar limit  $M \approx 1.4M_\odot$ .