

## School of Physics &amp; Astronomy

## PHS4200/PHS4021 Statistical Mechanics

## Lecture 5: Introduction to Quantum Statistics

## 5.1 Introduction

In previous lectures we examined various aspects of classical statistical mechanics, and applied the formalism to systems of distinguishable particles (e.g., an ideal classical gas described by Maxwell-Boltzmann statistics). However, many systems are intrinsically quantum mechanical, hence it is necessary to incorporate quantum statistics in order to describe a many particle system. Most notably in quantum statistics the energy levels are discrete and the symmetry requirements imposed on the many particle wavefunction lead to particles obeying either<sup>1</sup> Fermi-Dirac statistics or Bose-Einstein statistics. For example, under the exchange operator  $\hat{\rho}$ , the many particle wavefunction  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N)$  is either symmetric or antisymmetric, i.e.,

$$\hat{\rho}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = +\Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N) \quad (5.1)$$

or

$$\hat{\rho}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = -\Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_i, \dots, \mathbf{r}_N), \quad (5.2)$$

where the probability density is unaffected by particle interchange and  $\hat{\rho}^2 = \hat{\mathbb{I}}$ . The symmetric case corresponds to particles with integer spin ( $s = 0, 1, 2, \dots$ ) that obey Bose-Einstein statistics (bosons), whereas the antisymmetric case describes fermions, with half-integer spin ( $s = 1/2, 3/2, \dots$ ), which obey Fermi-Dirac statistics. The formal methods of quantum statistical mechanics will be developed in a later lecture; however, before we do so it is useful to first examine some of the salient features of quantum statistics.

## 5.2 Quantum Harmonic Oscillator

The quantum harmonic oscillator in one dimension has energy eigenvalues given by:

$$E_n = \left( n + \frac{1}{2} \right) \hbar \omega \quad (n = 0, 1, 2, \dots) \quad (5.3)$$

where the microstates of the oscillator are characterised by the principal quantum number  $n$ . The partition function for a single oscillator is:

$$Z(\beta, V, 1) = \sum_{n=0}^{\infty} e^{-\beta E_n} = e^{-\frac{1}{2}\beta \hbar \omega} \sum_{n=0}^{\infty} e^{-\beta n \hbar \omega}. \quad (5.4)$$

<sup>1</sup> It is possible to have particles whose statistics “interpolate” between Fermi-Dirac and Bose-Einstein statistics. For example in a two-dimensional system the permutation group, which describes the consequences of particle interchange, is replaced by the braid group. In this latter case we have particles that are neither fermions or bosons, but whose phase can adopt any value in the range  $[0, \pi]$ . These particles are referred to as anyons and their topological properties are of interest in quantum computing, see e.g.,

We recognise the sum in Eq. (5.4) as an infinite geometric series<sup>2</sup>, hence:

$$Z(\beta, V, 1) = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}} = \frac{1}{2\sinh(\frac{1}{2}\beta\hbar\omega)}. \quad (5.5)$$

For  $N$  non-interacting distinguishable quantum oscillators the partition function becomes

$$Z(\beta, V, N) = [Z(\beta, V, 1)]^N = [2\sinh(\frac{1}{2}\beta\hbar\omega)]^{-N}, \quad (5.6)$$

The Helmholtz free energy is readily calculated from:

$$\begin{aligned} F(T, V, N) &= -k_B T \ln Z(\beta, V, N) \\ &= Nk_B T \ln [2\sinh(\frac{1}{2}\beta\hbar\omega)] \\ &= Nk_B T \ln (e^{\frac{1}{2}\beta\hbar\omega} - e^{-\frac{1}{2}\beta\hbar\omega}) \\ &= Nk_B T \ln [e^{\frac{1}{2}\beta\hbar\omega} (1 - e^{-\beta\hbar\omega})] \\ &= \frac{1}{2} N\hbar\omega + Nk_B T \ln (1 - e^{-\beta\hbar\omega}). \end{aligned} \quad (5.7)$$

Note that the ground state energy of  $N$  non-interacting quantum oscillators is  $\frac{1}{2}N\hbar\omega$ . The thermodynamic parameters are obtained from the Helmholtz free energy (see Sec. 3.2.1):

$$\begin{aligned} p &= -\left(\frac{\partial F}{\partial V}\right)_{T, N} = 0, \\ S &= -\left(\frac{\partial F}{\partial T}\right)_{V, N} = Nk_B \left( \frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln[1 - e^{-\beta\hbar\omega}] \right), \\ \mu &= \left(\frac{\partial F}{\partial N}\right)_{T, V} = \frac{1}{2}\hbar\omega + k_B T \ln(1 - e^{-\beta\hbar\omega}). \end{aligned} \quad (5.8)$$

The internal energy of the system of oscillators is:

$$U = \langle E \rangle = \frac{\sum_{n=0}^{\infty} E_n e^{-\beta E_n}}{\sum_{n=0}^{\infty} e^{-\beta E_n}} = -\frac{\partial}{\partial \beta} \ln Z(\beta, V, N). \quad (5.9)$$

Substituting for the partition function (5.6), we obtain:

$$\begin{aligned} U &= -\frac{\partial}{\partial \beta} \ln Z(\beta, V, N) = -\frac{\partial}{\partial \beta} N \ln Z(\beta, V, 1) \\ &= -N \frac{\partial}{\partial \beta} \ln \left( \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right) \\ &= -N \frac{\partial}{\partial \beta} \left( -\frac{1}{2}\beta\hbar\omega - \ln[1 - e^{-\beta\hbar\omega}] \right) \\ &= N\hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right). \end{aligned} \quad (5.10)$$

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<sup>2</sup> The infinite geometric series is given by:

$$\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega} = 1 + e^{-\beta\hbar\omega} + e^{-\beta 2\hbar\omega} + \dots = \frac{1}{1 - e^{-\beta\hbar\omega}}.$$

This result can also be obtained directly from the internal energy (see Sec. 3.2.1), i.e.,

$$U = F + TS. \quad (5.11)$$

**Exercise 5.1:** Derive the thermodynamic parameters [i.e., Eq. (5.8)] from the Helmholtz free energy.

**Exercise 5.2:** Calculate the internal energy directly from Eqs. (5.8) and (5.11), and show that it is identical to the result obtained in Eq. (5.10).

**Exercise 5.3:** Re-analyse a system of  $N$  quantum oscillators which are indistinguishable. You will need to introduce the Gibbs factor  $1/N!$  to account for the indistinguishability of the oscillators.

It is useful to examine the internal energy  $U$  for some limiting cases. First consider the high temperature limit, for which the thermal energy is much greater than the energy spacing of the oscillators, i.e.,  $\beta\hbar\omega \ll 1$ . In this case Eq. (5.10) becomes:

$$\begin{aligned} U &= N\hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right) \\ &= N\hbar\omega \left( \frac{1}{2} + \frac{1}{(1 + \beta\hbar\omega + \frac{1}{2}(\beta\hbar\omega)^2 + \dots) - 1} \right) \\ &\approx N\hbar\omega \left( \frac{1}{2} + \frac{1}{\beta\hbar\omega} \right) \\ &\approx N\hbar\omega \left( \frac{1}{\beta\hbar\omega} \right) = Nk_B T. \end{aligned} \quad (5.12)$$

The result agrees with the equipartition theorem (see Sec. 2.3.2), as one would expect for a system of classical oscillators. However, in the limit of low temperatures, where  $\beta\hbar\omega \gg 1$ , we get a very different result, i.e.,

$$\begin{aligned} U &= N\hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right) \\ &\approx N\hbar\omega \left( \frac{1}{2} + e^{-\beta\hbar\omega} \right) \\ &\approx \frac{1}{2} N\hbar\omega. \end{aligned} \quad (5.13)$$

Equation (5.13) shows that as  $T \rightarrow 0$ , the oscillators are in their ground state, with zero point energy  $\frac{1}{2}N\hbar\omega$ . We also see that the entropy vanishes in the low temperature limit as required of the third law of thermodynamics, i.e.,

$$\lim_{T \rightarrow 0^+} S = \lim_{T \rightarrow 0^+} \left\{ Nk_B \left( \frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln[1 - e^{-\beta\hbar\omega}] \right) \right\} \rightarrow 0 \quad (\beta\hbar\omega \gg 1). \quad (5.14)$$

**Exercise 5.4:** Show that the entropy of a system of quantum oscillators vanishes in the low temperature limit.

### 5.2.1 Heat Capacity of a System of Quantum Oscillators

The results of Sec. 5.2 can be applied to the historically important problem of determining the heat capacity of a solid. We consider a solid as being composed of atoms of mass  $m$  that vibrate harmonically about their equilibrium positions. The Einstein model of a solid treats the atoms as independent three-dimensional oscillators, each having the same vibrational frequency  $\omega = \sqrt{K/m}$ , where the “spring constant”  $K$  specifies the interatomic potential energy. Using Eq. (5.10) we obtain an expression for the internal energy of a solid (in three dimensions):

$$U = 3N\hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right), \quad (5.15)$$

where there are  $3N$  degrees of freedom, hence the internal energy is just  $3N$  times that of a single quantum oscillator. The heat capacity at constant volume (and constant  $N$ ) is given by:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{V,N} = \left( \frac{\partial U}{\partial \beta} \right)_{V,N} \left( \frac{d\beta}{dT} \right) = -\frac{1}{k_B T^2} \left( \frac{\partial U}{\partial \beta} \right)_{V,N}. \quad (5.16)$$

Substituting for  $U$  from Eq. (5.15), we obtain:

$$\begin{aligned} C_V &= -\frac{1}{k_B T^2} \left( \frac{\partial U}{\partial \beta} \right)_{V,N} \\ &= -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \left\{ 3N\hbar\omega \left( \frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right) \right\} \\ &= -\frac{3N\hbar\omega}{k_B T^2} \frac{\partial}{\partial \beta} \{ (e^{\beta\hbar\omega} - 1)^{-1} \} \\ &= \frac{3N\hbar^2\omega^2}{k_B T^2} \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}. \end{aligned} \quad (5.17)$$

Equation (5.17) is conventionally written in term of the universal gas constant  $R = N_A k_B$  and the Einstein “temperature”  $\Theta_E = \hbar\omega/k_B$ , i.e.,

$$C_V = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}. \quad (5.18)$$

If the temperature is high  $\Theta_E/T \ll 1$ ,  $C_V \rightarrow 3R$ , which historically is known as the Dulong-Petit law. In the low temperature limit  $\Theta_E/T \gg 1$ , Eq. (5.18) reduces to:

$$\lim_{T \rightarrow 0^+} C_V = \lim_{T \rightarrow 0^+} \left\{ 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2} \right\} \rightarrow 3R \left( \frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T} \rightarrow 0. \quad (5.19)$$

Figure 5.1 shows a plot of  $C_V$  versus  $T$ .

**Example 5.1:** Estimate the Einstein temperature for lead and diamond, whose angular frequencies are approximately  $\omega_{Pb} = 4\pi \times 10^{12} \text{ s}^{-1}$  and  $\omega_D = 8\pi \times 10^{13} \text{ s}^{-1}$ , respectively.

## Solution

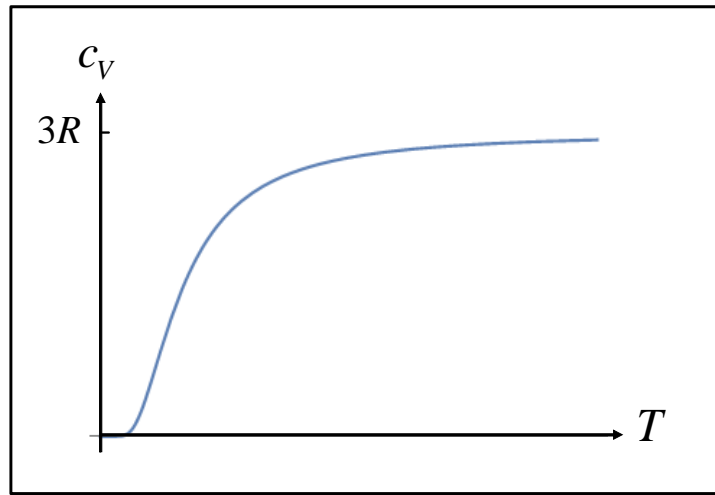
The Einstein temperature is  $\Theta_E = \hbar\omega/k_B$ , hence we have:

$$\Theta_E(Pb) = \frac{\hbar\omega_{Pb}}{k_B} = \frac{(1.055 \times 10^{-34} \text{ Js}) \times (4\pi \times 10^{12} \text{ s}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 96 \text{ K},$$

and

$$\Theta_E(Diamond) = \frac{\hbar\omega_D}{k_B} = \frac{(1.055 \times 10^{-34} \text{ Js}) \times (8\pi \times 10^{13} \text{ s}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 1921 \text{ K}.$$

This shows that at room temperature (300 K), diamond will have a specific heat that is much less than the classical value of  $3R$ . Of course the Einstein model of a solid, in which each atom oscillates with the same angular frequency, is a crude, albeit useful, approximation. A more sophisticated approach due to Debye<sup>3</sup>, treats the quantised lattice vibrations as a “gas” of phonons. The Debye model predicts that the specific heat  $C_V \propto T^3$ , as  $T \rightarrow 0^+$ , compared to the more rapid variation of the Einstein model (5.19).



**Figure 5.1:** Temperature dependence of the specific heat calculated according to Eq. (5.18).

## 5.3 Quantum Theory of Paramagnetism

In Sec. 4.4 we investigated the classical theory of paramagnetism in which the dipoles were able to adopt arbitrary orientations. However, the magnetic dipole moment  $\boldsymbol{\mu}$  and its component  $\mu_z$  (in the direction of the applied magnetic) field are discretised. The relationship between the magnetic moment of a dipole  $\boldsymbol{\mu}$  and its total angular momentum  $\mathbf{J}$  is:

$$\boldsymbol{\mu} = g \left( \frac{e\hbar}{2m_0c} \right) \mathbf{J} = g\mu_B \mathbf{J}, \quad (5.20)$$

where  $\mu_B = e\hbar/2m_0c$  is referred to as the Bohr magneton and the Lande  $g$ -factor is:

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}. \quad (5.21)$$

Here  $S$  and  $L$  are the spin and orbital angular momentum quantum numbers of the dipole. The

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<sup>3</sup> A discussion of the Debye model can be found at [https://en.wikipedia.org/wiki/Debye\\_model](https://en.wikipedia.org/wiki/Debye_model)

z-component of the dipole moment is specified by the magnetic quantum number  $m_J$  i.e.,

$$\mu_z = g\mu_B m_J \quad (m_J = -J, -J+1, \dots, J-1, J). \quad (5.22)$$

When the dipole is subjected to an external magnetic field it can only adopt  $2J+1$  discrete energy values given by:

$$E = -g\mu_B B m_J \quad (m_J = -J, -J+1, \dots, J-1, J). \quad (5.23)$$

where  $B = |\mathbf{B}|$  is the magnitude of the applied field. The canonical partition function of a system of  $N$  non-interacting magnetic dipoles is:

$$Z(\beta, B, N) = [Z(\beta, B, 1)]^N, \quad (5.24)$$

where  $Z(\beta, B, 1)$  is the partition function for a single dipole, i.e.,

$$[Z(\beta, B, 1)] = \sum_{m_J=-J}^{+J} e^{\beta g\mu_B B m_J}. \quad (5.25)$$

The sum in Eq. (5.25) is a finite geometric series, which is readily evaluated to give:

$$\begin{aligned} [Z(\beta, B, 1)] &= \sum_{m_J=-J}^{+J} e^{\beta g\mu_B B m_J} \\ &= e^{-\beta g\mu_B B J} + e^{\beta g\mu_B B (-J+1)} + \dots + e^{\beta g\mu_B B J} \\ &= \frac{e^{-\beta g\mu_B B J} (e^{\beta g\mu_B B (2J+1)} - 1)}{e^{\beta g\mu_B B} - 1} \\ &= \frac{e^{-\beta g\mu_B B J} e^{\beta g\mu_B B (2J+1)/2} (e^{\beta g\mu_B B (2J+1)/2} - e^{-\beta g\mu_B B (2J+1)/2})}{e^{\beta g\mu_B B /2} (e^{\beta g\mu_B B /2} - e^{-\beta g\mu_B B /2})} \\ &= \frac{\sinh(\beta g\mu_B B (J + \frac{1}{2}))}{\sinh(\frac{1}{2}\beta g\mu_B B)}. \end{aligned} \quad (5.26)$$

The average induced magnetisation is calculated from the partition function (5.24) as:

$$M = N\langle\mu_z\rangle = N \frac{\sum_{m_J=-J}^{+J} \mu_z e^{\beta g\mu_B B m_J}}{\sum_{m_J=-J}^{+J} e^{\beta g\mu_B B m_J}} = N \frac{1}{\beta} \frac{\partial}{\partial B} \ln Z(\beta, B, 1). \quad (5.27)$$

Substituting for the single dipole partition function (5.26) we obtain:

$$\begin{aligned} M &= N \frac{1}{\beta} \frac{\partial}{\partial B} \ln Z(\beta, B, 1) \\ &= N \frac{1}{\beta} \frac{\partial}{\partial B} \{ \ln [\sinh(\beta g\mu_B B (J + \frac{1}{2}))] - \ln [\sinh(\frac{1}{2}\beta g\mu_B B)] \} \\ &= Ng\mu_B \left[ \left( J + \frac{1}{2} \right) \coth[\beta g\mu_B B (J + \frac{1}{2})] - \frac{1}{2} \coth(\frac{1}{2}\beta g\mu_B B) \right] \\ &= Ng\mu_B JB_f(\beta g\mu_B B). \end{aligned} \quad (5.28)$$

where  $B_J(x)$  is referred to as the Brillouin function, which is defined as:

$$B_J(x) = \frac{1}{J} \left[ \left( J + \frac{1}{2} \right) \coth \left[ \left( J + \frac{1}{2} \right) x \right] - \frac{1}{2} \coth \left( \frac{1}{2} x \right) \right] \quad (x = \beta g \mu_B B). \quad (5.29)$$

Again we examine the limiting cases. First consider low temperatures (or large external fields), for which  $x = g \mu_B B / k_B T \gg 1$ , and the Brillouin function reduces to unity, i.e.,

$$\lim_{x \rightarrow \infty} B_J(x) \rightarrow \frac{1}{J} \left( J + \frac{1}{2} \right) - \frac{1}{2J} = 1 \Rightarrow M = N g \mu_B J. \quad (5.30)$$

For high temperatures (or small external fields)  $x = g \mu_B B / k_B T \ll 1$ . In this case the hyperbolic function:

$$\coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}}, \quad (5.31)$$

can be expanded to give:

$$\begin{aligned} \frac{e^x + e^{-x}}{e^x - e^{-x}} &= \frac{\left( 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + O(x^4) \right) + \left( 1 - x + \frac{1}{2!}x^2 - \frac{1}{3!}x^3 + O(x^4) \right)}{\left( 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + O(x^4) \right) - \left( 1 - x + \frac{1}{2!}x^2 - \frac{1}{3!}x^3 + O(x^4) \right)} \\ &\approx \frac{2 \left( 1 + \frac{1}{2}x^2 + O(x^4) \right)}{2 \left( x + \frac{1}{6}x^3 + O(x^4) \right)} \\ &= \left( 1 + \frac{1}{2}x^2 \right) \left( x + \frac{1}{6}x^3 \right)^{-1} \\ &= \frac{1}{x} + \frac{1}{3}x + O(x^3) \quad (x \ll 1). \end{aligned} \quad (5.32)$$

Using this approximation, the Brillouin function simplifies to:

$$\begin{aligned} B_J(x) &\rightarrow \frac{1}{J} \left\{ \left( J + \frac{1}{2} \right) \left[ \frac{1}{\left( J + \frac{1}{2} \right) x} + \frac{1}{3} \left( J + \frac{1}{2} \right) x \right] - \frac{1}{2} \left[ \frac{1}{\frac{1}{2}x} + \frac{1}{3} \left( \frac{x}{2} \right) \right] \right\} \\ &= \frac{1}{3} (J + 1) x. \end{aligned} \quad (5.33)$$

Substituting for  $x = \beta g \mu_B B$  into the expression for the magnetisation (5.28) we obtain:

$$M = N g \mu_B J B_J(x) = \frac{1}{3} N \beta g^2 \mu_B^2 J (J + 1) B = \frac{N g^2 \mu_B^2 J (J + 1) B}{3 k_B T}. \quad (5.34)$$

The magnetic susceptibility is calculated from:

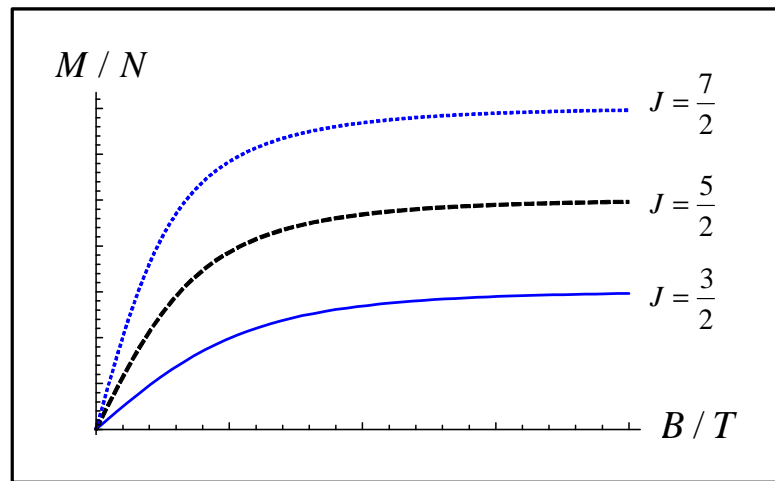
$$\chi(T) = \lim_{B \rightarrow 0} \left( \frac{\partial M}{\partial B} \right) = \frac{N g^2 \mu_B^2 J (J + 1)}{3 k_B T} = \frac{C}{T}, \quad (5.35)$$

where  $C$  is the Curie constant. Equation (5.35) is none other than Curie's law, which was derived in Sec. 4.4.1 within the classical Langevin theory of paramagnetism [c.f. Eq. (4.52)]. In Fig. 5.2

the magnetisation (5.28) is plotted for various values of the spin  $J$ . A study of spin paramagnetism<sup>4</sup> in  $\text{Cr}^{3+}$  ( $J = 3/2$ ),  $\text{Fe}^{3+}$  ( $J = 5/2$ ), and  $\text{Gd}^{3+}$  ( $J = 7/2$ ), shows excellent agreement between the experimental results and predictions of the Brillouin function. As the spin increases, the quantum mechanical dipole behaves more like the classical theory. In the limit  $J \rightarrow \infty$ , the dipole can effectively adopt any orientation and we recover the Langevin function (see Sec. 4.4), i.e.,

$$\lim_{J \rightarrow \infty} M = \lim_{J \rightarrow \infty} \{Ng\mu_B JB_J(x)\} \rightarrow Ng\mu_B JL(Jx) \quad (x = \beta g\mu_B B \ll 1). \quad (5.36)$$

**Exercise 5.5:** Show that the classical theory of paramagnetism is recovered in the limit  $J \rightarrow \infty$ .



**Figure 5.2:** The magnetisation per dipole as a function of  $B/T$ .

## 5.4 Quantum Statistics of Non-Interacting Particles

The statistical mechanics of non-interacting bosons is very different to non-interacting fermions. As noted in Sec. 5.1, when we exchange two identical fermions this leads to a sign change in the wavefunction, whereas there is no sign change for bosons. The spin of the particle and its statistics are related via the spin-statistics theorem<sup>5</sup>, so that fermions obey Fermi-Dirac statistics, whereas bosons are subject to Bose-Einstein statistics. To implement quantum statistics we restrict the ensemble sum, so that for fermions we sum over antisymmetric wavefunctions and for bosons we sum over symmetric wavefunctions. In practice this means that the partition function, for an  $N$  particle system, is restricted to a sum over the allowed quantum states.

To better understand what this means, consider an ideal system comprising non-interacting

<sup>4</sup> See Henry, W. E., *Phys. Rev.* **88**, 559-562 (1952). The original publication can be accessed at: <http://journals.aps.org/pr/pdf/10.1103/PhysRev.88.559>

<sup>5</sup> A discussion of the spin-statistics theorem can be found at: [https://en.wikipedia.org/wiki/Spin%E2%80%93statistics\\_theorem](https://en.wikipedia.org/wiki/Spin%E2%80%93statistics_theorem)

Pauli's original paper, titled "The Connection between Spin and Statistics", *Phys. Rev.*, **58**, 716-722 (1940), can be accessed at: <http://web.ihep.su/dbserve/compas/src/pauli40b/eng.pdf>



fermions or bosons (e.g., an ideal Fermi or Bose gas). The state of the system is specified by a set of occupation numbers  $\{n_i\}$ , where  $n_i$  is the number of particles in the  $i$ -th quantum state, whose energy is  $\epsilon_i$ . For example, the  $\alpha$ -th state of the system is described by the occupation numbers  $\alpha = (n_1, n_2, \dots, n_p, \dots)$ , where the allowed values for  $n_i$  are:

$$n_i = \begin{cases} 0, 1 & \text{fermions} \\ 0, 1, 2, \dots & \text{bosons.} \end{cases} \quad (5.37)$$

The total number of particles in the  $\alpha$ -th state is:

$$N_\alpha = \sum_i n_i \quad (5.38)$$

and the energy of the  $\alpha$ -th state is given by:

$$E_\alpha = \sum_i n_i \epsilon_i \quad (5.39)$$

In order to calculate the thermodynamics of non-interacting fermions or bosons, we need to evaluate the partition function. The canonical partition function for  $N$  non-interacting particles is:

$$Z(\beta, V, N) = \sum_{\{n_i\} = n_1, n_2, \dots, n_p, \dots} \exp\left(-\beta \sum_i n_i \epsilon_i\right), \quad (5.40)$$

subject to the constraint:

$$\sum_i n_i = N. \quad (5.41)$$

Unfortunately the equation of constraint (5.41) makes the evaluation of the canonical partition function (5.40) complicated. However, we can obviate the combinatorial problems imposed by the constraint by using the grand canonical partition function (see Sec. 3.4):

$$\Xi(\beta, V, N) = \sum_\alpha z^N e^{-\beta E_\alpha} = \sum_{\{n_i\}} \exp\left(-\beta \sum_i n_i (\epsilon_i - \mu)\right), \quad (5.42)$$

where the fugacity is defined by  $z = e^{\beta\mu}$ . In the following sections we will apply the grand canonical partition function (5.42) to determine the quantum distribution functions for fermions and bosons.

### 5.4.1 Fermi-Dirac Statistics

Let us consider  $N$  non-interacting fermions, where the sum in the grand partition function (5.42) is restricted to the occupation numbers  $n_i = 0$  or  $1$ , i.e.,

$$\begin{aligned} \Xi(\beta, V, N) &= \sum_{\{n_i = 0, 1\}} \exp\left(-\beta \sum_i n_i (\epsilon_i - \mu)\right) \\ &= \sum_{n_1=0}^1 \sum_{n_2=0}^1 \cdots \sum_{n_i=0}^1 \cdots \exp\left(-\beta \sum_i n_i (\epsilon_i - \mu)\right) \\ &= \sum_{n_1=0}^1 e^{-\beta n_1 (\epsilon_1 - \mu)} \sum_{n_2=0}^1 e^{-\beta n_2 (\epsilon_2 - \mu)} \cdots \sum_{n_i=0}^1 e^{-\beta n_i (\epsilon_i - \mu)} \cdots \\ &= \prod_i \left( \sum_{n_i=0}^1 e^{-\beta n_i (\epsilon_i - \mu)} \right) \\ &= \prod_i [1 + e^{-\beta (\epsilon_i - \mu)}]. \end{aligned} \quad (5.43)$$

The average number of fermions in the  $i$ -th state is given by:

$$\langle n_i \rangle = \frac{\sum_{n_1, n_2, \dots, n_i, \dots} n_i \exp\left(-\beta \sum_i n_i (\epsilon_i - \mu)\right)}{\sum_{n_1, n_2, \dots, n_i, \dots} \exp\left(-\beta \sum_i n_i (\epsilon_i - \mu)\right)}. \quad (5.44)$$

Equation (5.44) can also be written as:

$$\begin{aligned} \langle n_i \rangle &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \ln \left( \sum_{n_1, n_2, \dots, n_i, \dots} \exp\left(-\beta \sum_i n_i (\epsilon_i - \mu)\right) \right) \\ &= -\frac{1}{\beta} \frac{\partial \ln \Xi(\beta, V, N)}{\partial \epsilon_i}. \end{aligned} \quad (5.45)$$

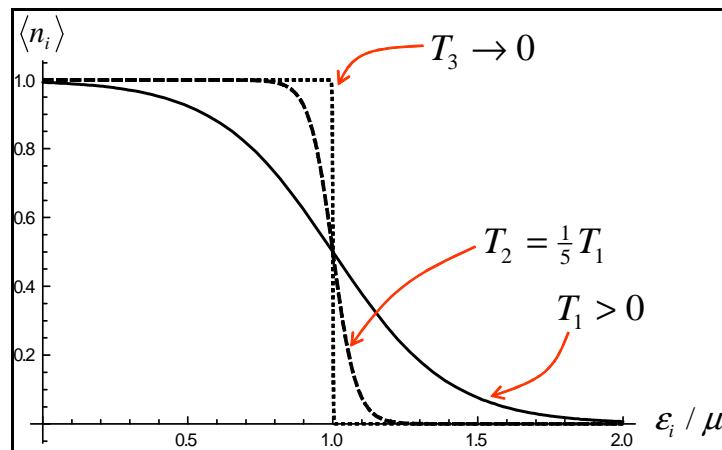
Substituting for the grand partition function (5.43) we obtain:

$$\begin{aligned} \langle n_i \rangle &= -\frac{1}{\beta} \frac{\partial \ln \Xi(\beta, V, N)}{\partial \epsilon_i} \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \ln \left( \prod_i [1 + e^{-\beta(\epsilon_i - \mu)}] \right) \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \sum_i \ln [1 + e^{-\beta(\epsilon_i - \mu)}] \\ &= \frac{e^{-\beta(\epsilon_i - \mu)}}{1 + e^{-\beta(\epsilon_i - \mu)}}. \end{aligned} \quad (5.46)$$

Upon re-arranging Eq. (5.46) we arrive at the Fermi-Dirac distribution:

$$f(\epsilon_i) = \langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}. \quad (5.47)$$

Figure 5.3 shows a plot of the Fermi function (i.e., the Fermi-Dirac distribution). Note that  $0 \leq \langle n_i \rangle \leq 1$ , as required by the Pauli exclusion principle. As  $T \rightarrow 0$  the Fermi function approaches a step function, so that states below the chemical potential are occupied. At 0 K the chemical potential is identified with the Fermi energy, with the corresponding Fermi level separating the occupied states from those states that are unoccupied. For  $T > 0$  the chemical potential represents the energy corresponding to an average occupancy of 0.5.



**Figure 5.3:** The Fermi function  $\langle n_i \rangle = f(\epsilon_i)$  for various temperatures.

### 5.4.2 Bose-Einstein Statistics

We now repeat the derivation in Sec. 5.4.1 for  $N$  non-interacting bosons, for which the occupation numbers are unrestricted, i.e.,  $n_i = 0, 1, 2, 3, \dots$ . The grand canonical partition function is:

$$\begin{aligned}
 \Xi(\beta, V, N) &= \sum_{\{n_i = 0, 1, 2, \dots\}} \exp\left(-\beta \sum_i n_i (\epsilon_i - \mu)\right) \\
 &= \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_i=0}^{\infty} \cdots \exp\left(-\beta \sum_i n_i (\epsilon_i - \mu)\right) \\
 &= \sum_{n_1=0}^{\infty} e^{-\beta n_1 (\epsilon_1 - \mu)} \sum_{n_2=0}^{\infty} e^{-\beta n_2 (\epsilon_2 - \mu)} \cdots \sum_{n_i=0}^{\infty} e^{-\beta n_i (\epsilon_i - \mu)} \cdots \\
 &= \prod_i \left( \sum_{n_i=0}^{\infty} e^{-\beta n_i (\epsilon_i - \mu)} \right).
 \end{aligned} \tag{5.48}$$

You should recognise the last summation as an infinite geometric series (see Footnote 2), which is readily summed to give:

$$\begin{aligned}
 \Xi(\beta, V, N) &= \prod_i \left( \sum_{n_i=0}^{\infty} e^{-\beta n_i (\epsilon_i - \mu)} \right) \\
 &= \prod_i \left( \frac{1}{1 - e^{-\beta (\epsilon_i - \mu)}} \right).
 \end{aligned} \tag{5.49}$$

The average number of bosons in the  $i$ -th state is given by:

$$\begin{aligned}
 \langle n_i \rangle &= -\frac{1}{\beta} \frac{\partial \ln \Xi(\beta, V, N)}{\partial \epsilon_i} \\
 &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \ln \left( \prod_i [1 - e^{-\beta (\epsilon_i - \mu)}]^{-1} \right) \\
 &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \sum_i \ln [1 - e^{-\beta (\epsilon_i - \mu)}]^{-1} \\
 &= +\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \sum_i \ln [1 - e^{-\beta (\epsilon_i - \mu)}] \\
 &= \frac{e^{-\beta (\epsilon_i - \mu)}}{1 - e^{-\beta (\epsilon_i - \mu)}}.
 \end{aligned} \tag{5.50}$$

Upon re-arranging Eq. (5.50) we arrive at the Bose-Einstein distribution:

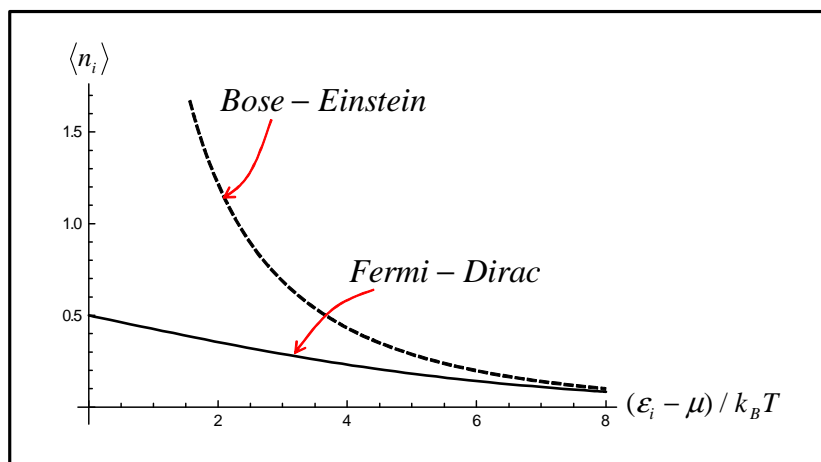
$$\langle n_i \rangle = \frac{1}{e^{\beta (\epsilon_i - \mu)} - 1}. \tag{5.51}$$

At high temperatures both the Fermi-Dirac distribution (5.47) and Bose-Einstein distribution (5.51) reduce to the classical Maxwell-Boltzmann distribution, i.e.,

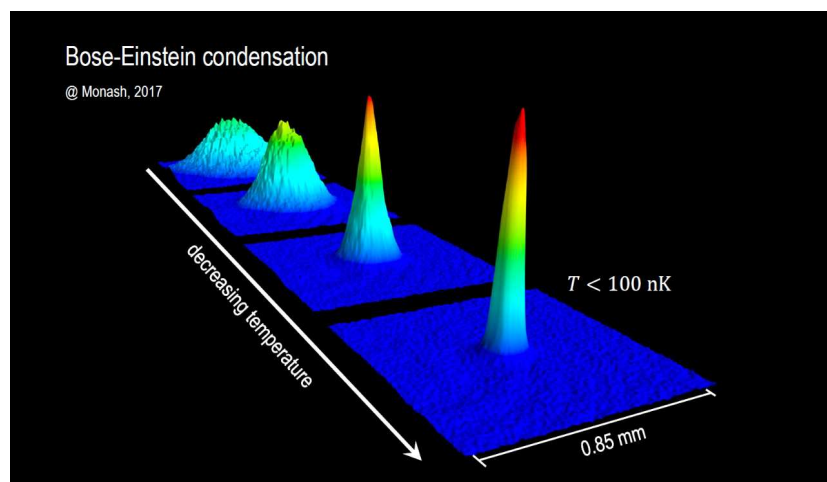
$$\langle n_i \rangle = \frac{1}{e^{\beta (\epsilon_i - \mu)} \pm 1} \xrightarrow{T \rightarrow \infty} e^{-\beta (\epsilon_i - \mu)}. \tag{5.52}$$

Equation (5.52) follows from  $e^{\beta (\epsilon_i - \mu)} \gg 1$ , which means that as  $T \rightarrow \infty$  (i.e.,  $\beta \rightarrow 0$ ) we must have  $-\beta \mu \gg 1$ , and the particle density  $\rho = \sum_i \langle n_i \rangle / V \rightarrow 0$ .

Although the Fermi-Dirac distribution and Bose-Einstein distribution appear to have a similar form, there are profound differences. Most notably the Bose-Einstein distribution diverges as  $\epsilon_i \rightarrow \mu$ , because the denominator in Eq. (5.51) vanishes (see Fig. 5.4). This means that a large number of bosons are able to be accommodated in a single particle state. The most spectacular example of this phenomenon is a Bose-Einstein condensate (BEC). Figure 5.5 shows Bose condensation of a dilute gas of *Rb* atoms produced in the spinor BEC laboratory at Monash.



**Figure 5.4:** The occupancy  $\langle n_i \rangle$  for Bose Einstein and Fermi-Dirac distributions. At  $\epsilon_i = \mu$ , the Fermi-Dirac distribution has an average occupancy of 0.5, whereas the Bose Einstein distribution diverges as  $\epsilon_i \rightarrow \mu$ .



**Figure 5.5:** Bose-Einstein condensation in a dilute gas of *Rb* atoms. At a temperature of less than 100 nK the condensation appears as a peak in the momentum distribution of atoms (Image courtesy of Russell Anderson and the Monash BEC Laboratory).

### 5.4.3 Photon Gas and Black Body Radiation

Photons obey Bose-Einstein statistics, with an unrestricted number of quanta in each state, i.e.,  $n = 0, 1, 2, 3, \dots$ . Photon numbers are not conserved and hence they are not subject to the constraint equation (5.41); consequently, for a photon gas the chemical potential<sup>6</sup>  $\mu = 0$ , i.e., it “costs” no

<sup>6</sup> A detailed discussion of the chemical potential for photons can be found at:  
<http://www.elp.uji.es/masterNNM/docencia/refs/2001%20Baierlein%20chem%20potential.pdf>

energy to add a photon to the gas. The distribution function for photons follows from setting  $\mu = 0$  in Eq. (5.51), i.e.,

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1}, \quad (5.53)$$

where the photon energy is  $\hbar \omega$ . Equation (5.53) is called the Planck distribution; it played a significant role in the birth of quantum mechanics, leading directly to the famous formula for the black body spectrum, to which we now turn our attention.

Consider a gas of indistinguishable photons (bosons) contained within a box of volume  $V$ . The gas is in thermal equilibrium with the walls of the box, which are held at temperature  $T$ . In this context photons are continuously absorbed and emitted by the walls of the box; consequently, the total number of photons is not constant. The state of each photon  $|\mathbf{k}, \sigma\rangle$  is specified by its  $\mathbf{k}$ -vector and polarisation index  $\sigma = 1, 2$ , where there are two possible polarisation states for each  $\mathbf{k}$ -vector. The average number of photons in each state is given by the Planck distribution (5.53). To proceed we need to calculate the number of states per unit volume (with a specified polarisation) that lie between  $\mathbf{k}$  and  $\mathbf{k} + d\mathbf{k}$ . This is readily determined by imposing periodic boundary conditions on the electromagnetic field (see Exercise 5.6), leading to:

$$k_x = \frac{2\pi n_x}{L_x}, \quad k_y = \frac{2\pi n_y}{L_y} \quad \text{and} \quad k_z = \frac{2\pi n_z}{L_z}, \quad (5.54)$$

where  $(n_x, n_y, n_z)$  are integers and  $(L_x, L_y, L_z)$  are the side lengths of the box. The number of states for which  $\mathbf{k}$  lies in the range between  $\mathbf{k}$  and  $\mathbf{k} + d\mathbf{k}$  is given by:

$$d^3n = dn_x dn_y dn_z = \left( \frac{L_x}{2\pi} dk_x \right) \left( \frac{L_y}{2\pi} dk_y \right) \left( \frac{L_z}{2\pi} dk_z \right) = \frac{V}{(2\pi)^3} d^3\mathbf{k} \quad (V = L_x L_y L_z). \quad (5.55)$$

For each polarisation state, the average number of photons per unit volume whose  $\mathbf{k}$ -vectors lie in the range between  $\mathbf{k}$  and  $\mathbf{k} + d\mathbf{k}$  is:

$$g(\mathbf{k}) d^3\mathbf{k} = \langle n \rangle \frac{d^3n}{V} = \frac{1}{e^{\beta \hbar \omega} - 1} \frac{d^3\mathbf{k}}{(2\pi)^3}. \quad (5.56)$$

It is evident that  $\mathbf{k}$ -vectors corresponding to points of equal energy lie on a sphere of radius  $k = |\mathbf{k}|$ , hence  $g(\mathbf{k})$  depends only on  $k$ , and Eq. (5.56) becomes:

$$g(k) d^3\mathbf{k} = \frac{1}{e^{\beta \hbar \omega} - 1} \frac{4\pi k^2 dk}{(2\pi)^3}. \quad (5.57)$$

Accounting for the two polarisation states ( $\sigma = 1, 2$ ) and using the well known dispersion relation,  $\omega = c|\mathbf{k}|$ , allows Eq. (5.57) to be expressed in terms of angular frequency:

$$g(\omega) d\omega = \frac{8\pi}{(2\pi)^3 c^3} \frac{\omega^2 d\omega}{e^{\beta \hbar \omega} - 1}. \quad (5.58)$$

The average energy per unit volume in the angular frequency range between  $\omega$  and  $\omega + d\omega$  is found by multiplying the average number of photons per unit volume (5.58) by the photon energy  $\hbar \omega$ . This defines the energy spectral density of black body radiation, i.e.,

$$\langle u(\omega, T) \rangle d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{e^{\beta \hbar \omega} - 1}. \quad (5.59)$$

Equation (5.59) is the celebrated Planck black body formula. Figure 5.6 show a plot of the energy spectral density as a function of wavelength for various temperatures.

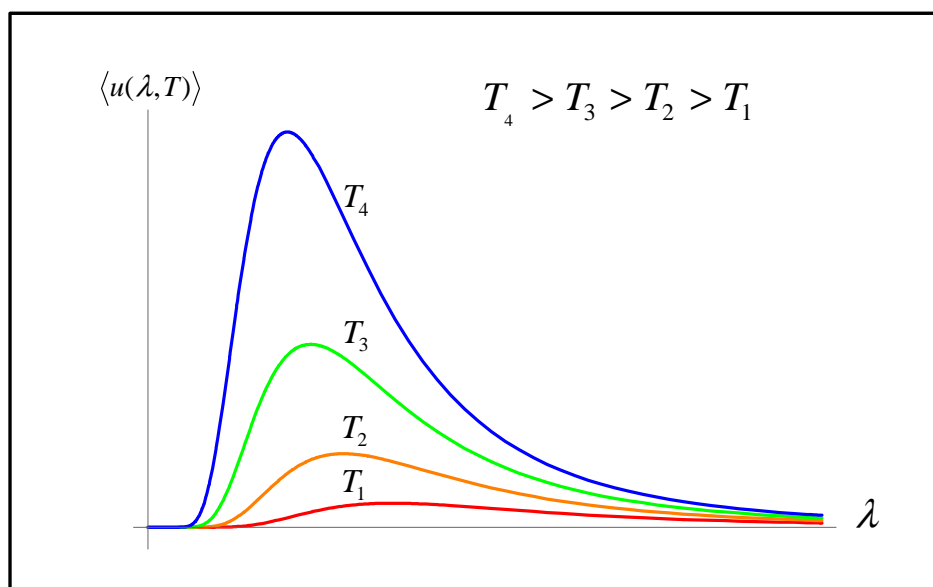
**Exercise 5.6:** Derive Eq. (5.54) by imposing periodic boundary conditions on the wavefunction.

*Hint:* Consider a plane wavefunction of the form  $\Psi_{\mathbf{k},\sigma}(\mathbf{r}) = \langle \mathbf{r} | \mathbf{k}, \sigma \rangle = A_{\sigma} e^{i\mathbf{k} \cdot \mathbf{r}}$ .

**Exercise 5.7:** Express the energy spectral density in terms of the wavelength  $\lambda$ . To convert from angular frequency to wavelength use the following relation:

$$\langle u(\omega, T) \rangle d\omega = \langle u(\omega, T) \rangle \frac{d\omega}{d\lambda} d\lambda = -\frac{2\pi c}{\lambda^2} \langle u(\lambda, T) \rangle d\lambda.$$

Note the appearance of the negative sign, which means that an increase in frequency corresponds to a decrease in wavelength.



**Figure 5.6:** The energy spectral density of a black body radiator for four different temperatures. Note how the maximum of  $\langle u(\lambda, T) \rangle$  shifts to lower wavelengths as the temperature is increased. This corresponds to the Wien displacement law  $\lambda_{\text{max}} T = \text{constant}$ .

If we integrate over all angular frequencies we obtain the average total energy density, i.e.,

$$\langle u(T) \rangle = \int_0^{\infty} \langle u(\omega, T) \rangle d\omega = \frac{\hbar}{\pi^2 c^3} \int_0^{\infty} \frac{\omega^3 d\omega}{e^{\beta \hbar \omega} - 1}. \quad (5.60)$$

It is convenient to introduce the dimensionless parameter  $x = \beta \hbar \omega$ , whence Eq.(5.60) becomes:

$$\langle u(T) \rangle = \frac{\hbar}{\pi^2 c^3} \left( \frac{k_B T}{\hbar} \right)^4 \int_0^{\infty} \frac{x^3 dx}{e^x - 1}. \quad (5.61)$$

The definite integral in Eq. (5.61) is evaluated<sup>7</sup> in Appendix A and equals  $\pi^4/15$ , which leads to the Stefan-Boltzmann law:

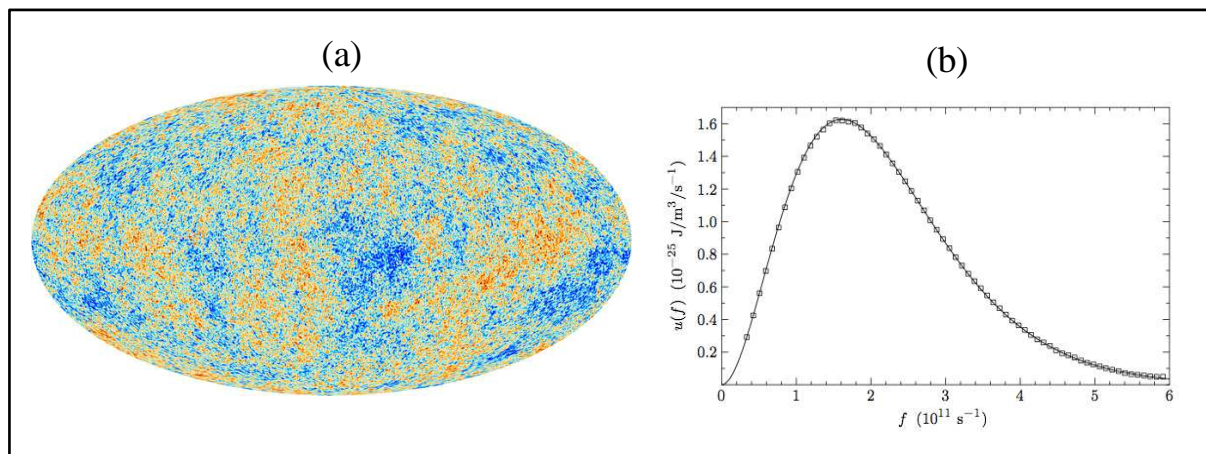
$$\langle u(T) \rangle = \sigma T^4, \quad (5.62)$$

where the Stefan-Boltzmann constant is  $\sigma = \pi^2 k_B^4 / 15 c^3 \hbar^3$ .

<sup>7</sup> Use Mathematica or see the following web site:

<https://stuff.mit.edu/afs/athena/course/8/8.03-esg/watkins/8.03/qthd.pdf>

There are many examples of thermal radiation in nature that are well described by the black body formula. Figure 5.7 (a) shows the observational data of the cosmic microwave background (CMB) radiation, acquired by the Planck satellite. In Fig. 5.7 (b) the Planck formula is fitted to the CMB, showing excellent agreement between observations and data based on a black body temperature of 2.725 K.



**Figure 5.7:** (a) CMB data from the Planck satellite. (b) A fit to the data based on the black body formula. (Images from [http://www.esa.int/Our\\_Activities/Space\\_Science/Planck](http://www.esa.int/Our_Activities/Space_Science/Planck)).

## Appendix A: Evaluation of the Planck Integral

The Planck integral in Eq. (5.61) is given by:

$$I = \int_0^{\infty} \frac{x^3 dx}{e^x - 1}. \quad (\text{A5.1})$$

Note that the integrand can be re-written as:

$$\frac{x^3}{e^x - 1} = \frac{x^3}{e^x(1 - e^{-x})} = \frac{x^3 e^{-x}}{(1 - e^{-x})} = x^3 \sum_{n=1}^{\infty} e^{-nx}, \quad (\text{A5.2})$$

where the last step exploits the summation formula for an infinite geometric series (see Footnote 2). Hence Eq. (A5.1) becomes:

$$I = \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \int_0^{\infty} x^3 \sum_{n=1}^{\infty} e^{-nx} dx = \sum_{n=1}^{\infty} \int_0^{\infty} x^3 e^{-nx} dx. \quad (\text{A5.3})$$

We can evaluate the last integral using integration by parts; however, there is an alternative much easier way to proceed by exploiting a “trick”, namely:

$$\int_0^{\infty} x^3 e^{-nx} dx = -\frac{d^3}{dn^3} \int_0^{\infty} e^{-nx} dx = -\frac{d^3}{dn^3} \left[ -\frac{1}{n} e^{-nx} \right]_0^{\infty} = -\frac{d^3}{dn^3} \left( \frac{1}{n} \right) = \frac{6}{n^4}. \quad (\text{A5.4})$$

Hence the Planck integral reduces to:

$$I = \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \sum_{n=1}^{\infty} \frac{6}{n^4} = 6\zeta(4), \quad (\text{A5.5})$$

where  $\zeta(s)$  is the Riemann zeta function, defined as:

$$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s} = \prod_{p \in \text{prime}} \left( 1 - \frac{1}{p} \right)^{-1}. \quad (\text{A5.6})$$

As an aside, we note that the Riemann zeta function is related to the distribution of primes - the famous Riemann hypothesis<sup>8</sup>.

There are a number of different ways to evaluate  $\zeta(4)$ . For completeness we will evaluate it using Fourier analysis. Recall that a function  $f(x)$  defined on the interval  $0 < x < \pi$  can be expressed as a Fourier series as:

$$f(x) = \frac{1}{2}a_0 + \sum_{n=1}^{\infty} (a_n \cos(nx) + b_n \sin(nx)), \quad (\text{A5.7})$$

where

$$a_0 = \frac{2}{\pi} \int_0^{\pi} f(x) dx, \quad a_n = \frac{2}{\pi} \int_0^{\pi} f(x) \cos(nx) dx \quad \text{and} \quad b_n = \frac{2}{\pi} \int_0^{\pi} f(x) \sin(nx) dx. \quad (\text{A5.8})$$

For reasons that will become evident let's choose  $f(x) = x^2$ . Since this is an even function we have:

$$x^2 = \frac{1}{2}a_0 + \sum_{n=1}^{\infty} a_n \cos(nx), \quad (\text{A5.9})$$

with

$$a_0 = \frac{2}{\pi} \int_0^{\pi} x^2 dx = \frac{2}{3}\pi^2 \quad \text{and} \quad a_n = \frac{2}{\pi} \int_0^{\pi} x^2 \cos(nx) dx = \frac{4}{n^2} \cos n\pi = \frac{4(-1)^n}{n^2}. \quad (\text{A5.10})$$

Therefore the Fourier series is:

$$x^2 = \frac{1}{3}\pi^2 + \sum_{n=1}^{\infty} \frac{4(-1)^n}{n^2} \cos(nx). \quad (\text{A5.11})$$

Setting  $x = \pi$  in Eq. (A5.11) gives the Riemann function  $\zeta(2) = \pi^2/6$ ; however, this is not the result we are after! To obtain the required result we exploit Parseval's theorem, i.e.,

$$\frac{1}{\pi} \int_{-\pi}^{\pi} |f(x)|^2 dx = \frac{1}{2} |a_0|^2 + \sum_{n=1}^{\infty} (|a_n|^2 + |b_n|^2), \quad (\text{A5.12})$$

so that:

$$\frac{1}{\pi} \int_{-\pi}^{\pi} x^4 dx = \frac{1}{2} \left( \frac{4\pi^4}{9} \right) + \sum_{n=1}^{\infty} \frac{16(-1)^{2n}}{n^4} \Rightarrow \frac{2}{5}\pi^4 = \frac{2}{9}\pi^4 + 16 \sum_{n=1}^{\infty} \frac{1}{n^4}, \quad (\text{A5.13})$$

which gives the Riemann function  $\zeta(4)$ , i.e.,

$$\zeta(4) = \sum_{n=1}^{\infty} \frac{1}{n^4} = \frac{\pi^4}{90}. \quad (\text{A5.14})$$

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<sup>8</sup> A very readable account of the Riemann hypothesis can be found in the book by Barry Mazur and William Stein, titled "*Prime Numbers and the Riemann Hypothesis*" (Cambridge University Press, 2016). A draft of this book is available online at:

<https://www.math.uh.edu/~saud/Number%20Theory/Mazur-Stein%20-%20Riemann%20Hypothesis.pdf>

A YouTube video of Mazur's lecture on the Riemann hypothesis is also available at:

[http://library.fora.tv/2014/04/25/Riemann\\_Hypothesis\\_The\\_Million\\_Dollar\\_Challenge](http://library.fora.tv/2014/04/25/Riemann_Hypothesis_The_Million_Dollar_Challenge)



Finally, we arrive at the result:

$$I = \int_0^{\infty} \frac{x^3 dx}{e^x - 1} = 6\zeta(4) = \frac{6\pi^4}{90} = \frac{\pi^4}{15}. \quad (\text{A5.15})$$

## References

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[http://home.basu.ac.ir/~psu/Books/%5BMehran\\_Kardar%5D\\_Statistical\\_Physics\\_of\\_Particles\(BookFi.org\).pdf](http://home.basu.ac.ir/~psu/Books/%5BMehran_Kardar%5D_Statistical_Physics_of_Particles(BookFi.org).pdf)
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