

Chapter 7

Bose Systems

In this chapter we apply the results of section 5.3 to systems of particles satisfying Bose-Einstein statistics. The examples are Black Body radiation (the photon gas), atomic vibration in solids (the phonon gas) and alkali atoms in traps and liquid ^4He (a Bose gas and fluid). Bosons in traps and the superfluid state of liquid ^4He is believed to be an example of Bose-Einstein condensation in which a large fraction of the Bosons occupy (condense into) the ground state.

7.1 Black Body Radiation

We are all familiar with the idea that hot objects emit radiation –a light bulb, for example. In the hot wire filament, an electron, originally in an excited state drops to a lower energy state and the energy difference is given off as a photon, ($\epsilon = h\nu = \epsilon_2 - \epsilon_1$). We are also familiar with the absorption of radiation by surfaces. For example, clothes in the summer absorb photons from the sun and heat up. Black clothes absorb more radiation than lighter ones. This means, of course that lighter colored clothes reflect a larger fraction of the light falling on them.

A black body is defined as one which absorbs all the radiation incident upon it –a perfect absorber. It also emits the radiation subsequently. If radiation is falling on a black body, its temperature rises until it reaches equilibrium with the radiation. At equilibrium it re-emits as much radiation as it absorbs so there is no net gain in energy and the temperature remains constant. In this case the surface is in equilibrium with the radiation and the temperature of the surface must be the same as the temperature of the radiation.

To develop the idea of radiation temperature we construct an enclosure having walls which are perfect absorbers (see Fig. 7.1). Inside the enclosure is radiation. Eventually this radiation reaches equilibrium with the enclosure walls, equal amounts are emitted and absorbed by the walls. Also, the amount of radiation travelling in each direction becomes equal and is uniform. In this

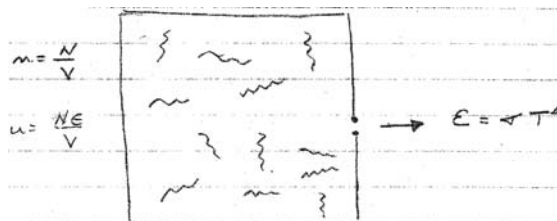


Figure 7.1: Isothermal Enclosure.

case the radiation may be regarded as a gas of photons in equilibrium having a uniform temperature. The enclosure is then called an isothermal enclosure.

An enclosure of this type containing a small hole is itself a black body. Any radiation passing through the hole will be absorbed. The radiation emitted from the hole is characteristic of a black body at the temperature of the photon gas. The properties of the emitted radiation is then independent of the materials of the wall provided they are sufficiently absorbing that essentially all radiation entering the hole is absorbed. This universal radiation is called Black Body Radiation.

An everyday example of a photon gas is the background radiation in the universe. This photon gas is at a temperature of about 5 K. Thus the earth's surface, at a temperature of about 300 K, is not in equilibrium with this gas. The earth is a net emitter of radiation (excluding the sun) and this is why it is dark at night and why it is coldest on clear nights when there is no cloud cover to increase the reflection of the earth's radiation back to the earth. A second example is a Bessemer converter used in steel manufacture containing molten steel. These vessels actually contain holes like the isothermal enclosure of Fig. 7.1. The radiation emitted from the hole is used in steel making to measure the temperature in the vessel, by means of an optical pyrometer.

Our model of black body radiation is a gas of non-interacting photons having energy related to their frequency ν and momentum \bar{p} by $\epsilon = h\nu = \bar{p}c$. Since photons can be regarded as relativistic (massless) particles, our model also represents a gas of relativistic finite mass particles for which $\epsilon^2 = \bar{p}^2c^2 + m^2c^4 \approx \bar{p}^2c^2$. What is the energy density, $u = U/V$, of this photon gas equilibrium? How does $u(T)$ depend upon T ? As in a gas of non-relativistic particles we expect a distribution over the possible energies and frequencies ($\epsilon = h\nu$) available to the photons, i.e.

$$u = \int_0^\infty u(\nu) d\nu$$

What is the spectral distribution $u(\nu)$? In terms of wavelength this is

$$u = \int_0^\infty d\lambda u(\lambda)$$

where $u(\lambda)$ is the energy density in wavelength range λ to $\lambda + d\lambda$. For a photon gas in the enclosure depicted in Fig. 7.1 what pressure does the photon gas

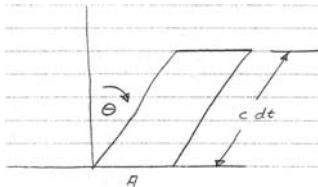


Figure 7.2: Number of photons absorbed by the wall from angle θ is $n dV = n (A c dt \cos \theta)$.

exert on the enclosure walls and what is the power per unit area, the emissive power, emitted from the hole?

To begin we answer these questions using kinetic theory and thermodynamics as far as possible. We then turn to statistical mechanics to complete the answer which forms a fine example of the interplay of thermodynamics and statistical mechanics. Also quantum ideas entered physics for the first time in the study of the photon gas. Planck in 1901 found mathematically that he could derive the observed $u(\lambda)$ if he summed over a discrete set of photon states ($\epsilon_n = nh\nu$) rather than integrating over a continuous set of states. This mathematical result was interpreted physically by Einstein in 1905, using the photoelectric effect, as discrete quanta of light (photons) each having energy $h\nu$.

7.1.1 Radiation Pressure and Emissive Power

We consider N photons in the enclosure of Fig. 7.1 each having momentum \bar{p} and energy $\epsilon = \bar{p}c = h\nu$. The number density is $n = N/V$ giving energy density $u = U/V = N\epsilon/V$. To obtain the pressure on the enclosure walls due to the photon gas we note that a single photon striking the wall at an angle θ from the normal, that is absorbed, transfers a momentum to the wall

$$\bar{p} \cos \theta. \quad (7.1)$$

The total number of such photons striking an area A of the wall (assuming for the moment they are all incident at angle θ) in time dt is

$$dN = n dV = n A c dt \cos \theta \quad (7.2)$$

Here $A (c dt \cos \theta)$ is the volume enclosing the photons each travelling at velocity c , that reach the wall in time dt (See Fig. 7.2). The momentum brought up to the wall in time dt is then,

$$\bar{p} \cos \theta dN = \bar{p} n A c dt \cos^2 \theta$$

The pressure (force per unit area = rate of change of momentum per unit area) due to these photons arriving at angle θ is

$$p(\theta) = \frac{1}{A} \frac{\bar{p} \cos \theta dN}{dt} = \bar{p} n \cos^2 \theta = u \cos^2 \theta \quad (7.3)$$

To find the total pressure we need the fraction of photons striking the

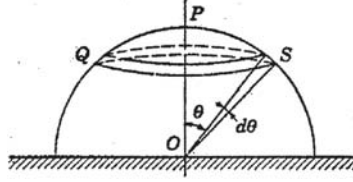


Figure 7.3: Hemisphere.

wall at angle θ . Since the photons are randomly distributed in direction we can represent their arrival (and departure) by the hemisphere depicted in Fig. 7.3 in which the fraction arriving from the angle θ is proportional to the surface area of the hemisphere subtended by the angle θ , divided by the total area of the hemisphere,

$$f(\theta) d(\theta) = \frac{2\pi r^2 \sin \theta d\theta}{2\pi r^2} = \sin \theta d\theta. \quad (7.4)$$

Here $2\pi r^2$ is the area of the hemisphere. The total pressure is then,

$$p = \int_0^{\pi/2} p(\theta) f(\theta) d\theta = 4 \int_0^{\pi/2} u \cos^2 \theta \sin \theta d\theta$$

or

$$p = \frac{1}{3} u \quad (7.5)$$

Here p is the final pressure if u is the average energy density.

We have made two compensating errors of 2 here. Firstly, there is an equal number of photons in the gas going toward and away from the wall in the volume dV in Fig. 7.2. Thus eq. (7.2) should be divided by 2. However, in equilibrium there is an equal number of photons emitted as absorbed so that the total momentum transferred to the surface is twice that due to arrival of photons alone. These two effects cancel to leave eq. (7.5) correct.¹

The Emissive Power emerging from the hole in the isothermal enclosure in Fig. 7.1 is defined as the power per unit area emitted from the hole. To calculate this we note that the energy brought up to a wall by a single photon is ϵ . The energy brought up to an area A by photons impinging on the wall at an angle θ in time dt is, from eq. (7.2),

$$\epsilon dN = \frac{1}{2} (\epsilon n) A c dt \cos \theta$$

the one half enters since one half of the photons in dV of Fig. 7.2 travel away from the wall. The power per unit area is then

$$\epsilon(\theta) = \frac{1}{A} \epsilon \frac{dN}{dt} = \frac{1}{2} u c \cos \theta$$

¹In Chapter 3 we found $p = 2/3 u$ for a perfect gas of classical non-interacting particles. This is true also for the perfect quantum gases. The difference of 2 enters in the relation between the velocity and energy. The pressure is really proportional to a product of momentum and velocity. In the relativistic gas case we have in eq. (7.3) $n(pv) = u$ while for nonrelativistic particles $n(\frac{1}{2}mv^2) = n(\frac{1}{2}pv) = u$.

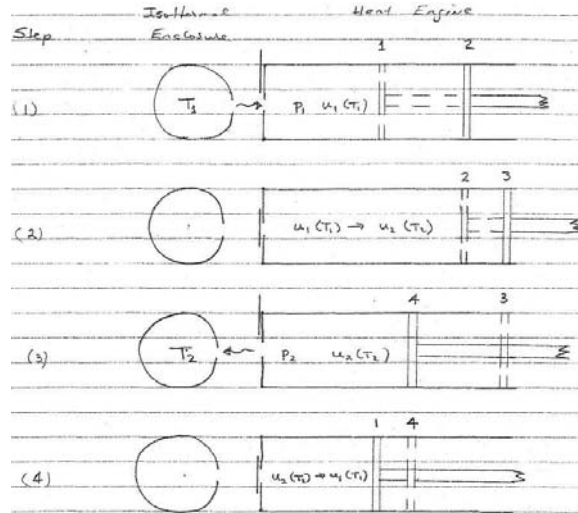


Figure 7.4: Heat Engine.

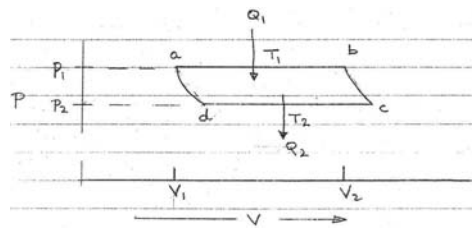


Figure 7.5: Carnot Cycle.

Averaging over all angles the total emissive power emerging from a hole in the enclosure wall is

$$E = \int_0^{\pi/2} d\theta f(\theta) \epsilon(\theta) = \frac{1}{4} cu \quad (7.6)$$

Using kinetic theory arguments we have related the radiation pressure eq. (7.3) and the emissive power eq. (7.6) to the energy density of the photon gas. We now employ thermodynamics to find the dependence of u on T .

7.1.2 Stefan - Boltzmann Law

In 1879 Stefan deduced the dependence of u on T from the observed emission power and found

$$u = a T^4 \quad (7.7)$$

where a is a constant. Boltzmann derived this relation using thermodynamics in 1884. Boltzmann used an isothermal enclosure containing a hole as a source

(and sink) for heat in a heat engine (see Fig. 7.4). He then took the engine through a complete Carnot cycle (see Fig. 7.5) and deduced the energy density from the fact that the total entropy change in the reversible cycle must be zero. We follow the steps in the cycle depicted in Fig. 7.4 and 7.5 briefly. The isothermal enclosure is assumed sufficiently large that it can emit and absorb radiation without substantial change in temperature.

Step (1) Open engine to black body at temperature T_1 . Make an isothermal expansion from volume V_1 to volume V_2 . Work done by the engine is

$$\delta W_1 = p_1 (V_2 - V_1) = \frac{1}{3} u_1 (V_2 - V_1) \quad (\text{i})$$

Change in Internal energy is

$$\delta U_1 = u_1 (V_2 - V_1)$$

Heat added from Isothermal enclosure is

$$\delta Q_1 = \delta U_1 + \delta W_1 = \frac{4}{3} u_1 (V_2 - V_1) \quad (\text{ii})$$

Step (2) Isolate engine from black body. Make isentropic expansion, T decreases from T_1 to T_2 in engine.

$$u_1(T_1) \rightarrow u_2(T_2).$$

Step (3) Lower temperature in black body to T_2 . Open engine to black body. Make an isothermal compression to point 4. Heat δQ_2 is transferred to the black body at temperature T_2 .

Step (4) Isolate engine from black body. Make isentropic compression back to V_1 . T increases from T_2 to T_1 and the internal energy returns to its original value.

A thermodynamic analysis of the cycle gives

(1) Net work done by engine (conservation energy)

$$\delta W = \delta Q_1 - \delta Q_2 \quad (\text{iii})$$

The net work done is also given by the area enclosed in the cycle in Fig. 7.5. If the change in pressure is small, this is

$$\delta W = \delta p (V_2 - V_1) = \frac{1}{3} \delta u (V_2 - V_1) \quad (\text{iv})$$

(2) Second Law requires

$$dQ_1 = T_1 dS_1 \quad - \text{entropy change in Step (1)}$$

$$dQ_2 = T_2 dS_2 \quad - \text{entropy change in Step (2)}$$

and, since the steps are reversible, the total change in entropy must be zero at the end of the cycle,

$$dS_1 = dS_2 .$$

Then

$$\frac{\delta W}{\delta Q_1} = 1 - \frac{\delta Q_2}{\delta Q_1} = 1 - \frac{T_2 dS_2}{T_1 dS_2} = \frac{T_1 - T_2}{T_1} = \frac{\delta T}{T_1}$$

From (ii) and (iv)

$$\frac{\delta W}{\delta Q_1} = \frac{1}{4} \frac{\delta u}{u_1} = \frac{\delta T}{T_1}$$

and

$$u = aT^4$$

Thus the Stefan - Boltzmann law can be derived using thermodynamics alone and the emissivity is

$$E = \frac{1}{4} cu = \frac{1}{4} ca T^4 = \sigma T^4 \quad (7.8)$$

Here $\sigma = 0.567 \times 10^{-7}$ joules/m² K⁴ sec is Stefan's constant. We cannot, however determine a or σ thermodynamically or the spectral distribution. For these we turn to statistical mechanics.

7.1.3 The Spectral Distribution

(a) Historical Aside

The distribution of energy density over wavelength, $u(\lambda)$, in a photon gas having total energy density

$$u = \int_0^\infty d\lambda u(\lambda) \quad (7.9)$$

holds a special place in the development of quantum mechanics. Wien proposed, making specific assumptions about the absorption and emission of photons at the enclosure walls, that the spectral distribution should take the form

$$u(\lambda) = \frac{c_1}{\lambda^5} e^{-c_2/\lambda T} \quad (7.10)$$

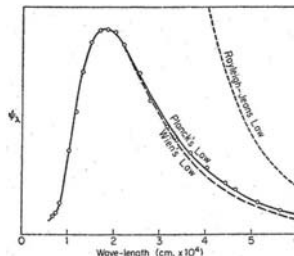
where c_1 and c_2 were undetermined constants. Rayleigh in 1900 and Jeans in 1905 proposed the expression

$$u(\lambda) = \frac{8\pi}{\lambda^4} kT \quad (7.11)$$

on general grounds which we can readily reproduce here.

From our discussion in section 4.1, the number of photons (particles) we expect in a wavelength range λ to $\lambda + d\lambda$ is

$$dN(\lambda) = \bar{n}(\lambda) g(\lambda) d\lambda \quad (7.12)$$

Figure 7.6: The Black Body Spectral Distribution Law, $u(\lambda)$.

Here $\bar{n}(\lambda)$ is the expected occupation of energy states $\epsilon = h\nu = hc/\lambda$ and $g(\lambda)$ is the density of states. The energy density in this wave length interval is then

$$u(\lambda) d\lambda = \frac{1}{V} \epsilon(\lambda) dN(\lambda) = \frac{1}{V} \epsilon(\lambda) \bar{n}(\lambda) g(\lambda) d\lambda \quad (7.13)$$

To obtain $g(\lambda)$ we recall that the density of states per momentum interval is $g(p) = V 4\pi p^2/h^3$. Then using the de Broglie relation $p = h/\lambda$

$$g(p) dp = V \pi 4 \lambda^{-4} d\lambda \quad (7.14)$$

Here we have dropped the negative sign in $dp = -h/\lambda^2 d\lambda$ since the density of states must be a positive number. Also there are two transverse polarizations (two states) possible at each wavelength so that

$$g(\lambda) d\lambda = 2 g(p) dp = V 8\pi \lambda^{-4} d\lambda$$

In this development we have used the de Broglie relation which came long after the work of Rayleigh and Jeans. However, $g(\lambda)$ can be obtained by considering the states available to oscillators (which emit radiation) but the argument is longer as we shall see in section 7.2.2.

Expressed in terms of the photon frequency, via $\nu = c/\lambda$,

$$g(\nu) d\nu = \frac{V 8\pi}{c^3} \nu^2 d\nu \quad (7.15)$$

Employing this density of states, Rayleigh and Jeans proposed $\bar{n} = 1$, using the idea of a priori equal occupation probability of each state, and set $\epsilon(\lambda) = kT$, using the equipartition theorem value for the energy of an oscillator. More correctly we should say $\bar{\epsilon} = \epsilon(\lambda) \bar{n}(\lambda) = kT$. This gave the Rayleigh-Jeans law

$$u(\lambda) = \frac{8\pi kT}{\lambda^4}.$$

From Fig. 7.6 we see this agrees with the observed $u(\lambda)$ at wavelenght only.

Originally, Planck thought the Wien expression was correct since it agreed with experiment. Planck also did not agree with equipartition and he could derive eq. (7.10) assuming the oscillator energy depended on its frequency

($\epsilon = h\nu = hc/\lambda$) and \bar{n} given by the Boltzmann factor, $\bar{n} \propto \epsilon^{-\beta\epsilon} = e^{-\frac{\beta hc}{\lambda}}$, so that

$$u(\lambda) = \frac{1}{V} \bar{\epsilon}(\lambda) g(\lambda) = c_1/\lambda^5 e^{-c_2/\lambda kT} \quad (7.16)$$

However, more accurate experiments by Lummer and Pringsheim and by Rubens and Kurlbaum showed that Wien's expression did not fit the data at long wavelength. Planck then made his pioneering assumption that the oscillator energy levels were discrete and given by

$$\epsilon_s = sh\nu \quad , \quad s = 0, 1, 2, \dots$$

The derivation then followed exactly that leading to (4.58) except that the zero point energy ($1/2 h\nu$) was not included. Without the zero point energy, the expected energy of N photons having frequency ν is

$$U(\nu) = N \bar{\epsilon}(\nu) = N \frac{h\nu}{(e^{\beta h\nu} - 1)}$$

Substituting this energy into eq. (7.16) leads to Planck's radiation law

$$u(\nu) = \frac{1}{V} \bar{\epsilon}(\nu) g(\nu) = \frac{8\pi}{c^3} \frac{h\nu}{(e^{\beta h\nu} - 1)} \nu^2$$

or

$$u(\lambda) = \frac{8\pi hc}{\lambda^5} \frac{1}{(e^{\frac{\beta hc}{\lambda}} - 1)} \quad (7.17a)$$

(b) Statistical Mechanics

To derive Planck's radiation law directly from our statistical mechanics of section 5.3, we note that number of photons in the gas is not fixed. The photons are absorbed and re-emitted by the enclosure walls. Since the photons are non-interacting it is by this absorption and re-emission that equilibrium is maintained in the gas. Since, also the free energy $F(T, V, N)$ is constant in equilibrium (at constant T and V) while N varies it follows that $\partial F/\partial N = 0$, that is

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = 0$$

We obtain the important result that if the number of particles is freely variable in equilibrium, the chemical potential is zero.

The photon gas is then a Bose gas with $\mu = 0$ so that the canonical partition function is given directly from (5.24) as

$$Z = \mathcal{Z} = \prod_{s=1}^r (1 - e^{-\beta\epsilon_s})^{-1} \quad (7.18)$$

and the expected Bose occupation is

$$\bar{n}_s = (\epsilon^{\beta\epsilon_s} - 1)^{-1}. \quad (7.19)$$

Using $\epsilon = h\nu$ we then obtain from eq. (7.19) and the density of states eq. (7.15),

$$u(\nu) = \frac{1}{V} \epsilon(\nu) \bar{n}(\nu) g(\nu)$$

or

$$u(\nu) = \frac{8\pi}{c^3} \frac{h\nu}{(e^{\beta h\nu} - 1)} \nu^2 \quad (7.17b)$$

which is Planck's Radiation Law.

We may also recover Wien and Rayleigh-Jeans laws as limits of Planck's law,

(a) Long wavelength, $\frac{hc}{kT\lambda} \ll 1$

Here

$$\bar{\epsilon} = \frac{hc/\lambda}{(\epsilon^{\frac{hc}{kT\lambda}} - 1)} \approx kT$$

and eq. (7.17a) becomes

$$u(\lambda) = \frac{1}{V} \bar{\epsilon}(\lambda) g(\lambda) \approx \frac{8\pi}{\lambda^4} kT \quad (7.20)$$

which is the Wien law valid at long wavelength.

(b) Short Wavelength, $\frac{hc}{kT\lambda} \gg 1$

Here

$$\bar{\epsilon} = \frac{hc}{\lambda} e^{-\frac{hc}{kT\lambda}}$$

and eq. (7.20) becomes

$$u(\lambda) = \frac{1}{V} \bar{\epsilon}(\lambda) g(\lambda) \approx \frac{8\pi hc}{\lambda^5} e^{-\frac{hc}{kT\lambda}} \quad (7.21)$$

which is the Wien law valid at short wavelength with the constants c_1 and c_2 of eq. (7.10) determined. These approximations are depicted in Fig. 7.6

Employing our statistical mechanics we readily obtained Planck's radiation law. We may also derive the Stefan - Boltzmann law eq. (7.8), for

$$u = \int_0^\infty d\nu u(\nu) = \frac{8\pi}{c^3} \int_0^\infty d\nu \frac{h\nu}{(e^{\beta h\nu} - 1)} \nu^2$$

Introducing $x = \beta h\nu$, this reduce to

$$u = \frac{8\pi k^4}{(hc)^3} \int_0^\infty dx \frac{x^3}{(e^x - 1)} T^4 = aT^4$$

with

$$a = \frac{8\pi}{(hc)^3} k^4 \int_0^\infty dx \frac{x^3}{(e^x - 1)} = \frac{8\pi k^4}{(hc)^3} \frac{\pi^4}{15} \quad (7.22)$$

In this way we obtain, using statistical mechanics, a law derived previously using thermodynamics including all the numerical factors. This gives Stefan's constant σ in

$$E = \frac{1}{4} ca T^4 = \sigma T^4$$

as

$$\sigma = \frac{2\pi^5}{15} \frac{ck^4}{(hc)^3} = 5.67 \times 10^{-5} \frac{\text{erg}}{\text{cm}^2 \text{ sec K}^4} \quad (7.23)$$

A measurement of σ could then be used, for example, to determine Planck's constant. Planck in fact determined h as the constant needed in his radiation law eq. (7.20) to fit the observed spectral distribution law. This gave him the value $h = 6.55 \times 10^{-27}$ erg.sec which compares with the present value of

$$h = 6.625 \times 10^{-27} \text{ erg.sec}$$

7.1.4 Thermodynamic Properties

We may calculate all the thermodynamic properties of black body radiation using statistical mechanics through the partition function Z and

$$F = -kT \log Z$$

where Z is given by eq. (7.18). This is the basic method of statistical thermodynamics. The aim is to reproduce all the thermodynamic properties with all factors and constants evaluated. This gives

$$\begin{aligned} F &= -kT \log \prod_{s=1}^r (1 - e^{-\beta\epsilon_s})^{-1} \\ &= -kT \sum_{s=1}^r \log (1 - e^{-\beta\epsilon_s})^{-1} \\ &= -kT \ 2 \int \frac{d\Gamma}{h^3} \log (1 - e^{-\beta\epsilon})^{-1} \end{aligned} \quad (7.24)$$

where the ϵ_s are the single photon states and the factor of 2 arises from the two polarizations available to each photon. This can be integrated in a variety of ways. Perhaps the most direct is to integrate over phase space ($d\Gamma = dV \ 4\pi p^2 \ dp$) and write $\epsilon = pc$. Introducing the dimensionless variable $x = \beta\epsilon = \beta pc$ the Helmholtz free energy is

$$F = -\frac{1}{3} \left\{ -\frac{8\pi k^4}{(hc)^3} \int_0^\infty d(x)^3 \log(1 - e^{-x}) \right\} VT^4 \quad (7.25)$$

The dimensionless integral here can be transformed into that appearing in the constant a of eq. (7.22) by an integration by parts, i.e.

$$I = -\int_0^\infty d(x)^3 \log(1 - e^{-x}) = -\left. (x)^3 \log(1 - e^{-x}) \right|_0^\infty + \int_0^\infty x^3 d[\log(1 - e^{-x})]$$

The first term vanishes since

$$(a) \lim_{x \rightarrow \infty} x^3 \log(1 - e^{-x}) \approx \lim_{x \rightarrow \infty} x^3 e^{-x} \rightarrow 0$$

$$(b) \lim_{x \rightarrow 0} x^3 \log(1 - e^{-x}) \approx \lim_{x \rightarrow 0} x^3 \log x \rightarrow 0$$

and

$$I = \int_0^{\infty} dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$$

Comparing eqs. (7.22) and (7.25)

$$F = -\frac{1}{3} aVT^4 \quad (7.26)$$

From F we may determine all other thermodynamic properties by differentiation. For example, the entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = 4/3 aVT^3 \quad (7.27)$$

The internal energy is

$$U = F + TS = -\frac{1}{3} aVT^4 + 4/3 aVT^4 = aVT^4$$

given an energy density

$$u = \frac{1}{V} U = aT^4 \quad (7.28)$$

identical to eq. (7.7) as required. The pressure is

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{1}{3} aT^4 = \frac{1}{3} u$$

in agreement with eq. (7.5). The Gibbs free energy is

$$G = F + pV = -\frac{1}{3} aVT^4 + \frac{1}{3} aVT^4 = 0$$

This is zero as required since $G = \mu N$ and the chemical potential $\mu = 0$. We may use these expressions to further verify thermodynamic consistency, for example that $C_V = T\left(\frac{dS}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$.

In summary, we have obtained the spectral distribution eq. (7.17) from the Bose function \bar{n}_s of eq. (7.19) in much the same way as we obtained the Maxwell-Boltzmann distribution for a classical gas. The only other required ingredient was the density of states eq. (7.15). We have also obtained all the thermodynamic properties using the partition function Z .

7.2 Phonons in Solids

7.2.1 Introduction

A solid is a collection of N atoms in an ordered array. The ordered array is called a lattice and we could imagine building up the solid by placing an atom on

each lattice point. The points represent the equilibrium positions of the atoms in the solid. Since the atoms have thermal energy they vibrate about these equilibrium lattice points. At low temperature the vibrational displacements $\vec{u}(\ell)$ ($\ell = 1, \dots, N$) of the atoms away from their lattice points is small. In a typical metal at room temperature the RMS vibrational amplitude is about 5% of the interatom spacing. At the melting point of the metal this increases to about 15% of the interatom spacing.

When the displacements of the atoms are small we may approximate the complicated interatomic forces by a simple harmonic force pulling each atom back to its lattice point. Each atom is harmonically bound to its lattice point. In this case the Hamiltonian for the solid is

$$H = \frac{1}{2} \sum_{\ell\alpha} m \left(\frac{du_{\alpha}(\ell)}{dt} \right)^2 + \frac{1}{2} \sum_{\ell\alpha, \ell'\beta} \phi_{\alpha\beta}(\ell\ell') u_{\alpha}(\ell) u_{\beta}(\ell') \quad (7.29)$$

This looks rather formidable but here $u_{\alpha}(\ell)$ is the displacement of atom ℓ , in direction α , $\phi_{\alpha\beta}(\ell\ell')$ is the harmonic restoring force constant and H is simply the Hamiltonian for a set of N coupled oscillators. The ϕ can be obtained from the interatomic forces between the atoms but are often simply regarded as parameters.

To simplify H we can express it in terms of “normal coordinates” Q_q which are related to the displacements and in which H becomes decoupled. In these coordinates, the Hamiltonian (eq. 7.29) is

$$H = \frac{1}{2} \sum_{q=1}^{3N} \left[\left(\frac{dQ_q}{dt} \right)^2 + \omega_q^2 Q_q^2 \right] \quad (7.30)$$

The H now describes $3N$ independent oscillators, one oscillator for each original coordinate $u_{\alpha}(\ell)$. The characteristic frequency of each oscillator, ω_q , is related to the ϕ but for our purposes we again regard them as parameters. Eqs. (7.29) and (7.30) represent atomic vibration in the harmonic approximation.

The Hamiltonian (7.30) is our starting point or model of atomic vibration in solids. The discussion above simply serves to indicate its origin. Since each oscillator in eq. (7.30) is independent we can treat each as a statistically independent system. Our model is therefore a gas of independent oscillators. The total energy will then be a simple sum of each oscillator energy. We recall that the energy levels of a harmonic oscillator having characteristic frequency ω_q are

$$\epsilon_q = \hbar\omega_q \left(n_q + \frac{1}{2} \right) \quad n_q = 0, 1, 2, \dots \quad (7.31)$$

where n_q is the quantum number labeling the state². In the ground state, ($n_q = 0$) the oscillator q has energy $\epsilon_q = \frac{1}{2}\hbar\omega_q$. The total energy at $T = 0$ K is

²Note that each independent oscillator can be treated separately exactly as we treated the vibration of a single diatomic molecule in Chapter 4 (compare Eqs. (7.31) and (4.56)). We could calculate the single oscillator partition function as in eq. (4.57) and the vibrational

$\sum_q \frac{1}{2} \hbar \omega_q$, called the zero point energy. At finite T the total vibrational energy of the solid is

$$E_S(n_1 \dots n_q \dots) = \sum_{q=1}^{3N} \epsilon_q = \sum_{q=1}^{3N} \hbar \omega_q (n_q + \frac{1}{2}) \quad (7.32)$$

This expression of the vibrational energy of the atoms suggests a new interpretation. When the oscillator q is in the n_q^{th} state we could say there are n_q excitations each of energy $\hbar \omega_q$ excited. Each such excitation is called a phonon. In fact an analysis of the atomic displacements associated with each oscillator coordinate shows that each excitation represents a wave of atomic displacements travelling down the solid. The name phonon is based on the analogy of these displacement waves having discrete energy $\hbar \omega_q$ and photons having discrete energy $\hbar \omega$. Hence the energy (eq. 7.32) is interpreted as the energy of n_q such phonons plus the zero point energy. The total vibrational energy (eq. 7.32) of the solid is then regarded as a gas of n_1 phonons of energy $\hbar \omega_1$, n_2 phonons of energy $\hbar \omega_2$ and so on. It is called a gas since the phonons are independent and non-interacting. This is then an alternative model of the vibrational energy and has more physical meaning than the set of oscillators. It is clearly very similar to the photon gas we considered in section 7.1.

7.2.2 Energy and Specific Heat

The average energy or internal energy associated with the phonon gas is given by eq. (7.32) with each n_q replaced by its thermal average value or expected value at a temperature T .

$$U(T) = \sum_q \bar{\epsilon}_q = \sum_q \hbar \omega_q (\bar{n}_q + 1/2) \quad (7.33)$$

Since the phonons have zero spin they are bosons. Also since the number of phonons in the gas is completely unrestricted and variable, the chemical potential is zero. In the phonon gas interpretation this suggests immediately that the expected number of phonons of energy $\hbar \omega_q$ is given by the Bose function

$$\bar{n}_q = (e^{\beta \hbar \omega_q} - 1)^{-1} \quad (7.34)$$

However, rather than use this result, let us consider the independent harmonic oscillator model and calculate the average energy $\bar{\epsilon}_q$ for each oscillator. This will serve to demonstrate the use of the Boltzmann factor and the equivalence of the

partition function of the solid would be a simple product of these single oscillator partition functions eq. (4.57)

$$Z = \prod_{q=1}^{3N} Z_q = \prod_{q=1}^{3N} (\epsilon^{\frac{1}{2} \beta \hbar \omega_q} - \epsilon^{-\frac{1}{2} \beta \hbar \omega_q})$$

Here the $\hbar \omega_q$ of each oscillator replaces the characteristic energy $h\nu$ of the diatomic molecule.

two models. Since each oscillator is statistically independent the probability of observing it in state having energy ϵ_q is proportional to the Boltzmann factor, $\exp(-\beta\epsilon_q)$. The average energy of oscillator q is then,

$$\begin{aligned}\bar{\epsilon}_q &= \sum_{\epsilon_q} \epsilon_q e^{-\beta\epsilon_q} / \sum_{\epsilon_q} e^{-\beta\epsilon_q} \\ &= \sum_{n_q=0}^{\infty} \hbar\omega_q(n_q + 1/2) e^{\beta\hbar\omega_q(n_q+1/2)} / \sum_{n_q=0}^{\infty} e^{-\beta\hbar\omega_q(n_q+1/2)} \\ &= -\frac{\partial}{\partial\beta} \log \sum_{n_q=0}^{\infty} e^{-\beta\hbar\omega_q(n_q+1/2)} = \frac{\hbar\omega_q}{(e^{\beta\hbar\omega_q} - 1)} + 1/2 \hbar\omega_q\end{aligned}\quad (7.35)$$

Thus the internal energy is

$$U(T) = \sum_q \frac{\hbar\omega_q}{(e^{\beta\hbar\omega_q} - 1)} + 1/2 \sum_q \hbar\omega_q \quad (7.36)$$

in agreement with eqs. (7.33) and (7.34).

At $T = 0$, $\bar{n}_q = 0$ and there are no phonons excited. Only the zero point energy of the solid remains. As we heat the crystal, phonons are excited and the expected number n_q of phonons increases. Clearly, from eq. (7.34) if the phonon energies are large fewer phonons are excited at a given temperature.

The specific heat due to the atomic vibration can be calculated by evaluating $U(T)$ and using

$$C_V = \left(\frac{dU}{dT}\right)_V$$

The C_V will clearly depend on the spectrum of characteristic phonon frequencies ω_q . Today it is possible to calculate the frequency spectrum directly from a model of the interatomic forces for many solids, for example for the solid inert gases and the alkali metals. Comparison of the calculated and observed specific heats then serves as a test of the interatomic force models. In many cases, in the past, it was not possible to calculate the ω_q directly. For these cases we write the sum in $U(T)$ as a general integral over the frequency spectrum

$$U(T) = \int_0^{\omega_D} d\omega \bar{\epsilon}(\omega) g(\omega) \quad (7.37)$$

Here $\bar{\epsilon}(\omega) = \hbar\omega(\bar{n}(\omega) + 1/2)$ and $g(\omega)$ is the density of frequencies in the range ω to $\omega + d\omega$ and ω_D is the maximum frequency follows from the periodicity of the crystal. We now need a model for $g(\omega)$ and ω_D .

In 1912 Debye proposed the approximation

$$g(\omega) = K\omega^2 \quad (7.38)$$

for the density of states where K is a constant. This follows for an elastic continuum in which the discrete nature of the atoms is ignored. It also follows

from filling up phase space since this leads to $g(\omega) \propto \omega^2$. This is the density of states we obtained in eq. (7.13) for the photon gas (section 7.1.3) using phase space counting, for example. In fact in the Debye model eq. (7.37) the energy of the phonon gas is identical to that of the photon gas except for the limit to the frequencies of ω_D .

The remaining parameter in the Debye theory is ω_D . The constant K can be determined by noting that there are $3N$ frequencies in the crystal.

Then

$$\int_0^{\omega_D} g(\omega) d\omega = 3N \quad (7.39)$$

and substituting eq. (7.38) gives

$$K = \frac{9N}{\omega_D^3}$$

The thermal energy is

$$U(T) = \frac{9N}{\omega_D^3} \int_0^{\omega_D} d\omega \hbar\omega (n(\omega) + 1/2) \omega^2$$

which we express in terms of a dimensionless integral, introducing $x = \beta\hbar\omega$,

$$U(T) = \frac{9N(kT)^4}{(\hbar\omega_D)^3} \left[\int_0^{x_D} \frac{x^3 dx}{(e^x - 1)} + 1/2 \int_0^{x_D} x^3 dx \right]$$

or

$$U(T) = 9NkT \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^3 dx}{(e^x - 1)} + \frac{9}{8} R\theta_D \quad (7.40)$$

The remaining parameter in the theory,

$$\theta_D = \frac{\hbar\omega_D}{k}, \quad (7.41)$$

is called the Debye Temperature. Here $E_Z = 9/8 R\theta_D$ is the zero point energy in the Debye Model. The thermal energy depends solely on the ratio of θ_D to T . As in the diatomic molecule the strength of the interatomic forces in the solid are described by the single characteristic Debye temperature. This can clearly only be an approximation for a solid so we should not expect the Debye model to describe $U(T)$ exactly. A large Debye temperature indicates strong interatomic forces while a low Debye temperature suggests weak interatomic forces. Some typical values of θ_D obtained by fitting the Debye expression for C_V to experiment are shown in table 7.1.

	Cu	Ag	Au	Al	Na	W	C*	Si	Ar
$\theta_D(K)$	345	226	165	415	155	350	2220	640	84

* diamond

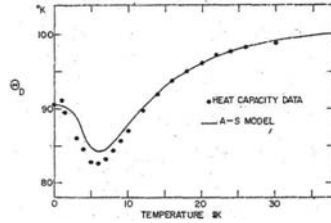


Figure 7.7: The variation in θ_D with temperature required for the Debye C_V fit experiment. (From R.A. Cowley et al. Phys. Rev. 150, 487 (1968))

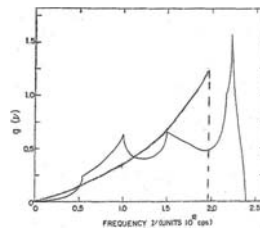


Figure 7.8: The Debye density states $g(\omega)$ compared to an exact calculation in potassium. (From Cowley et al.)

If the Debye approximation to $g(\omega)$ holds, $U(T)$ given by eq. (7.40) should fit experiment with a constant value of θ_D . In fact it is necessary to allow θ_D to vary with T to get eq. (7.40) to fit experiment showing that the Debye theory fits only approximately. This is shown, for example, for potassium, in Fig. 7.7. The Debye theory is now so engrained in solid state physics that measurements of C_V are often presented as values of $\theta_D(T)$ v.s. T . A comparison of the Debye approximation and an explicit calculation of $g(\omega)$ for solid are compared in Fig. 7.8.

We consider now the high and low temperature limits of the Debye theory.

(a) Low temperatures, $T \ll \theta_D$

In this case we take the limit in eq. (7.40) as $\theta_D/T \rightarrow \infty$ and the integral there is just $\pi^4/15$ giving a thermal energy per mole,

$$U = \frac{3\pi^4}{5} R \frac{T^4}{\theta_D^3}$$

and

$$C_V = \frac{12}{5} \pi^4 R \left(\frac{T}{\theta_D}\right)^3. \quad (7.42)$$

This gives us the famous Debye expression for the low temperature C_V , proportional to T^3 . In this limit the phonon gas energy becomes identical to that of photon gas, where the energy density is $u = aT^4$ (see eq. 7.22). Only the value of the constant of proportionality (given by θ_D) fixing the vibrational frequencies differs.

(b) High temperatures, $T \gg \theta_D$

In this case θ_D/T is small so that x in eq. (7.40) is always small. We may then expand $(e^x - 1)^{-1}$ as $(1 - x)^{-1}$. The thermal energy per mole is then

$$U = 9 RT \left(\frac{T}{\theta_D}\right)^3 \frac{1}{3} \left(\frac{\theta_D}{T}\right)^3 = 3 RT \quad (7.43)$$

and $C_V = 3R$, which is the classical result, the Dulong-Petit law.

In practice we find eq. (7.42) does not hold until $T \lesssim \theta_D/50$ which from table 7.1 corresponds to a very low temperature. Also the specific heat of most metals does not become classical until well above room temperature. Also C_V is $C_V = 3R$ only in the harmonic approximation. Usually C_V differs from $3R$ in real solid due to anharmonic contributions.

7.2.3 The Free Energy

The partition function of the solid in the harmonic approximation discussed above can be readily evaluated as

$$Z = \sum_S e^{-\beta E_S} \quad (7.44)$$

where E_S is given by eq. (7.32). The possible states E_S can be enumerated by summing over all possible values of n_q in eq. (7.32),

$$\begin{aligned} Z &= \sum_{n_{q_1}, n_{q_2}} \dots e^{-\beta \sum_q \hbar \omega_q (n_q + \frac{1}{2})} = \sum_{n_{q_1}, n_{q_2}} \dots \prod_q e^{-\beta \hbar \omega_q (n_q + \frac{1}{2})} \\ &= \prod_q \left(\sum_{n_q=0}^{\infty} e^{-\beta \hbar \omega_q (n_q + \frac{1}{2})} \right) = \prod_q e^{-\frac{1}{2} \beta \hbar \omega_q} (1 - e^{-\beta \hbar \omega_q})^{-1} \\ &= \prod_q (e^{\frac{1}{2} \beta \hbar \omega_q} - e^{-\frac{1}{2} \beta \hbar \omega_q})^{-1} \end{aligned} \quad (7.45)$$

The partition function for the phonon gas is a product of partition functions for each independent oscillator,

$$Z = Z_{q_1} Z_{q_2} \dots$$

Each Z_q is the same as the vibrational partition function we obtained in section for a single diatomic molecule having characteristic frequency $\hbar \omega_q = h\nu$. The total Z is a simple product because the total energy E_S is a sum of oscillator energies. Thus Z is a product in the same way that Z for an atom having internal degrees of freedom of Z_q is a product of a Z for each independent degree of freedom.

To complete the model we should really add to E_S the potential energy, ϕ , of the crystal with the atoms fixed at their lattice points. Then

$$\begin{aligned} Z &= e^{-\beta\phi} \sum_S e^{-\beta E_S} \\ &= e^{-\beta\phi} \prod_q 2 \sinh \left(\frac{1}{2} \beta \hbar \omega_q \right) \end{aligned} \quad (7.46)$$

and the Helmholtz free energy is

$$F = -kT \log Z = \phi + kT \log 2 \sinh \left(\frac{1}{2} \beta \hbar \omega_q \right) \quad (7.47)$$

and all other thermodynamic functions follow by differentiation. For example,

$$\begin{aligned} U &= \frac{\partial}{\partial \beta} (\beta F) = \frac{\partial}{\partial \beta} \left(\beta \phi + \sum_q \left[\log (1 - e^{-\beta \hbar \omega_q}) + \frac{1}{2} \beta \hbar \omega_q \right] \right) \\ &= \phi + \sum_q \hbar \omega_q \left(\bar{n}_q + \frac{1}{2} \right) \end{aligned} \quad (7.48)$$

which agrees with eq. (7.36). The entropy is

$$S = \frac{1}{T} (U - F) = k \sum_q \left[\beta \hbar \omega_q \bar{n}_q - \log (1 - e^{-\beta \hbar \omega_q}) \right] \quad (7.49)$$

which depends only on the thermal vibrational energy. This clearly goes to zero as $T \rightarrow 0$.

7.3 Bose Gas

As a third example of Bose statistics we consider an ideal gas of Bose particles. This is a gas of any integral spin (e.g. zero spin) particles at a temperature low enough that quantum effects are important. Quantum effects become important when the thermal wavelength $\lambda_T = (h^2/2\pi m k T)^{1/2}$ of the particles is comparable or greater than the interparticle spacing, i.e. $n \lambda_T^3 \gtrsim 1$. The prime physical example is a gas of ^4He atoms. In fact the ^4He - ^4He interatomic interaction is strong enough that the gas condenses into a liquid at low temperature, below 4.2 K. In spite of this, liquid ^4He properties are often compared with similar properties in the perfect Bose gas.

In 1924 Einstein proposed that a Bose gas at low temperature would undergo a “condensation” in which a macroscopic or large fraction of the particles condense into the lowest energy single particle state (the zero momentum state). This Bose-Einstein condensation was a logical consequence of the new statistics introduced by Bose. Although there is not yet a fully satisfactory theory of

liquid ${}^4\text{He}$ this condensation is observed in liquid ${}^4\text{He}$ at $T = T_\lambda = 2.17$ K. At T_λ a fraction of atoms begin to condensate into the condensate state. At $T = 0$ K 7.25 ± 0.75 % of the fluid is in the condensate. This condensation is the fundamental origin of superfluidity in liquid ${}^4\text{He}$ at T_λ . The superfluid component in liquid ${}^4\text{He}$ arises from the component of the liquid condensed into the zero momentum state.

Similarly, Bose-Einstein condensation (BEC) is observed in gases of alkali atoms confined in harmonic traps. In this case the Bosons are in an external confining potential $U(r)$, the gas is dilute, $n(r) = N(r)/V \sim 10^8$ atoms/cm³, and the gas density $n(r)$ varies with distance r from the center of the trap. The gas can be cooled to extremely low temperature ($T \sim 5 \times 10^{-9}$ K) where essentially 100 % of the atoms condense into the lowest energy state, in this case a harmonic oscillator state. We now discuss this condensation and its relation to liquid ${}^4\text{He}$.

7.3.1 Ideal Bose Gas and Bose Einstein Condensation

Specifically, we consider a uniform gas of N non-interacting Bosons confined to a volume V at constant number density $n = N/V = 1/v$. There is no external potential $U(r)$ confining the N Bosons in V except the walls of the container –i.e. $U(r) = 0$. Such a gas cannot be realized in practice at low temperature since the equilibrium state of Bosons is liquid if $U(r) = 0$. However, a uniform Bose gas serves as an outstanding model for Bose gases in harmonic magnetic traps where $U(r) = \frac{1}{2}m\omega_0^2 r^2$ and ω_0^2 is the trap frequency. The uniform Bose gas also shows several features displayed by uniform liquid ${}^4\text{He}$ such as BEC, superflow if there is weak interaction, entropy that is carried by particles in excited states above the condensate only.

The Bose function (5.26) gives the number of Bosons in each single particle state ϵ_s as

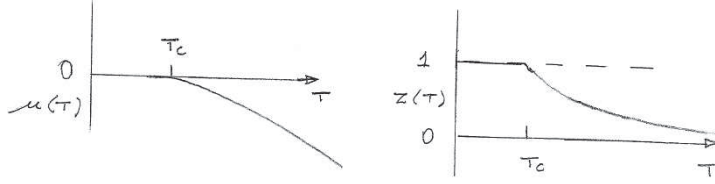
$$n_s = (e^{\beta(\epsilon_s - \mu)} - 1)^{-1}.$$

Since n_s must be positive ($n_s \geq 0$) and we may choose the energy scale so that the lowest single particle energy is zero ($\epsilon_0 = 0$), we must have

$$\mu < 0.$$

If $\mu > 0$ and $\epsilon_0 = 0$, then $n_0 = (e^{-\beta\mu} - 1)^{-1}$ would be negative which is unphysical.

In a classical gas, we found that the chemical potential was large and negative, $\mu = -kT \log(1/n\lambda_T^3)$. In the classical limit, $\lambda_T = (h^2/2\pi mkT)^{\frac{1}{2}}$ is short, much less than the diameter of an atom. As the temperature is lowered λ_T increases, $n\lambda_T^3$ increases and μ increases toward zero, its maximum value. The fugacity z defined by $z = e^{\beta\mu}$ is, in the classical limit, just $z = n\lambda_T^3$ (classical limit only). As temperature is decreased and μ goes from a large negative number to zero, $z = e^{\beta\mu}$ goes from zero to its maximum value of 1, $0 \leq z \leq 1$. This dependence is displayed in Fig. 7.9.

Figure 7.9: The chemical potential μ and fugacity $z = e^{\beta\mu}$ for a Bose gas.

The total number density in the gas is

$$\frac{N}{V} = \frac{1}{V} \sum_s n_s = \frac{1}{V} \sum_s \left(e^{\beta(\epsilon_s - \mu)} - 1 \right)^{-1}. \quad (7.50)$$

Since N/V is constant, $\mu(T)$ and $z(T) = e^{\beta\mu}$ must change with temperature to maintain N/V constant.

Similarly, the thermodynamic properties can be obtained from the Grand partition function

$$\Omega = -pV = -kT \log \mathcal{Z} \quad (7.51)$$

where $\mathcal{Z} = \sum_N \sum_S e^{-\beta(E_S - \mu N)}$, the gas energy is $E_S = \sum_s n_s \epsilon_s$ and $N = \sum_s n_s$. In section 5.3 we found $\log \mathcal{Z} = -\sum_s \log(1 - ze^{-\beta\epsilon_s})$ so that

$$\frac{p}{kT} = -\frac{1}{V} \sum_s \log(1 - ze^{-\beta\epsilon_s}). \quad (7.52)$$

Other thermodynamic properties can be obtained by differentiating Ω (i.e. $\log \mathcal{Z}$). We note particularly that the gas energy is

$$U = \sum_N z^N \sum_S E_S e^{-\beta E_S} = \sum_s n_s \epsilon_s$$

so that

$$U = -\frac{\partial}{\partial \beta} (\log \mathcal{Z})_{z,n} \quad (7.53)$$

Note that the expression is defined as differentiation at constant z . In general $z(T)$ is a function of temperature.

The remainder of the development consists of evaluating N/V and $\log \mathcal{Z}$ and exploring their properties. For Bosons in a box, the density of states s is,

$$\begin{aligned} \sum_s &= \int ds = \int d\Gamma \left(\frac{ds}{d\Gamma} \right) = \frac{1}{h^3} \int \int d^3r d^3p \\ &= \frac{1}{h^3} \int d^3r \int 4\pi p^2 dp \end{aligned}$$

Since $U(r) = 0$, we can integrate over the volume directly and independently of p to obtain $\int d^3r = V$. However, if $U(r) \neq 0$, then $\epsilon = p^2/2m + U(r)$ and

$p^2 = 2m[\epsilon - U(r)]$ and the integration over r and p is coupled, as we shall see for Bosons confined in a trapping potential, $U(r)$. For $U(r) = 0$, we have $p = (2m\epsilon)^{\frac{1}{2}}$ and the sum over states gives the number of states up to energy ϵ as

$$\sum_s = V \int_0^\epsilon d\epsilon' \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} \epsilon'^{\frac{1}{2}} = N(\epsilon)$$

and the density of states is

$$g(\epsilon) = \frac{dN(\epsilon)}{d\epsilon} = V \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} \quad (7.54)$$

as we obtained before. Thus for a uniform gas of Bosons we obtain

$$\frac{N}{V} = \frac{1}{\lambda_T^3} \frac{1}{(\sqrt{\pi}/2)} \int_0^\infty dx \frac{x^{\frac{1}{2}}}{(\frac{1}{z}e^x - 1)} = \frac{1}{\lambda_T^3} g_{3/2}(z) \quad (7.55)$$

and

$$\begin{aligned} \frac{p}{kT} &= -\frac{1}{\lambda_T^3} \frac{1}{(\sqrt{\pi}/2)} \int_0^\infty dx x^{\frac{1}{2}} \log(1 - ze^{-x}) \\ &= \frac{1}{\lambda_T^3} \frac{1}{(3/2)(\sqrt{\pi}/2)} \int_0^\infty dx \frac{x^{\frac{3}{2}}}{(\frac{1}{z}e^x - 1)} = \frac{1}{\lambda_T^3} g_{5/2}(z) \end{aligned} \quad (7.56)$$

The second expression for p/kT is obtained by an integration by parts. The functions $g_\nu(z)$ are defined as

$$g_\nu(z) \equiv \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{(\frac{1}{z}e^x - 1)} \quad (7.57)$$

where $\Gamma(\nu)$ is the Gamma function. We will encounter $\Gamma(\nu)$ for $\nu = \frac{1}{2}$ integers only for which $\Gamma(\frac{1}{2}) = \sqrt{\pi}$ and $\Gamma(\nu + 1) = \nu\Gamma(\nu)$, i.e. $\Gamma(\frac{3}{2}) = \frac{1}{2}\Gamma(\frac{1}{2}) = \frac{\sqrt{\pi}}{2}$. The $g_\nu(z)$ are often denoted the Bose gas functions. For the case $z = 1$ (i.e. for temperatures $T \leq T_c$), the $g_\nu(z)$ reduce to the Riemann zeta functions, $g_\nu(z = 1) = \zeta(\nu)$. A simple and useful representation of the $g_\nu(z)$ is obtained by expanding the denominator in eq. (7.57) in a power series giving

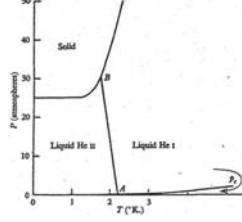
$$g_\nu(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^\nu} = z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \dots \quad (7.58)$$

Eq. (7.58) may also be taken as the definition of $g_\nu(z)$. It is particularly useful when derivatives of $g_\nu(z)$ are sought or the classical limit $z \rightarrow 0$ is taken.

7.3.2 Bose-Einstein Condensation

From eq. (7.55), the product of the number density and λ_T^3 is

$$n\lambda_T^3 = g_{3/2}(z). \quad (7.59)$$

Figure 7.10: The phase diagram of ${}^4\text{He}$.

We consider first constant $n = N/V$. In the high temperature, classical limit of the Bose gas, where $z \rightarrow 0$, we have from the series expression (7.58) $g_{3/2}(z) = z$ so that $n\lambda_T^3 = z = e^{\beta\mu}$. This is the classical result for μ and z —where $n\lambda_T^3 \ll 1$. As temperature is lowered, λ_T^3 increases and LHS of eq. (7.59) increases. The RHS of eq. (7.59) must similarly increase. However, the RHS reaches a maximum value at $z = 1$, where $g_{3/2}(z = 1) = \zeta(\frac{3}{2}) = 2.612$. At temperatures below this critical temperature T_c , λ_T^3 continues to increase and eq. (7.59) is no longer fulfilled. We might say that all N of the Bosons in $(\frac{N}{V})$ can no longer be accommodated in the result $n\lambda_T^3 = 2.612$. Specifically, all N Bosons can no longer be accommodated in the states $\epsilon > 0$ since the DOS $g(\epsilon)$ given by eq. (7.54) includes only the $\epsilon > 0$ states. In eq. (7.54) because of the $\epsilon^{\frac{1}{2}}$, the ground (zero energy) state ϵ_0 has zero weight and is not included in eq. (7.59).

At $T = T_c$, we can just accommodate all N atoms in the excited ($p > 0$, $\epsilon > 0$) single particle states. At constant n , T_c is determined as the lowest temperature at which eq. (7.59) is fulfilled, i.e. T_c is defined by

$$n\lambda_{T_c}^3 = 2.612. \quad (7.60)$$

Below T_c to accommodate all N of the Bosons we must explicitly include the zero momentum state ($p = 0$, $\epsilon = 0$) in eq. (7.59). That is, we have for $T < T_c$,

$$n = n_{\text{ex}} + n_0 = \frac{2.612}{\lambda_T^3} + n_0 \quad (7.61)$$

Where n_{ex} is the density of Bosons in the $p \neq 0$ states at $T < T_c$. Below T_c , since we have included excited states only in eq. (7.59), $n_{\text{ex}} \lambda_T^3 = 2.612$. Clearly $n_{\text{ex}} \rightarrow 0$ as $\lambda_T \rightarrow \infty$ at $T \rightarrow 0$. Indeed from $n\lambda_{T_c}^3 = 2.612 = n_{\text{ex}} \lambda_T^3$ and from eq. (7.61) we have

$$1 = \frac{n_{\text{ex}}}{n} + \frac{n_0}{n} = \frac{\lambda_{T_c}^3}{\lambda_T^3} + \frac{n_0}{n}$$

or

$$\frac{n_0}{n} = \frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \quad (7.62)$$

N_0/N is defined as the condensate fraction.

Thus at constant n , we begin to get a macroscopic fraction N_0/N in the $p = 0$ state at a temperature $T = T_c$ with T_c given by eq. (7.60). Bose-Einstein

condensation (BEC) begins at T_c . At $T < T_c$ the fraction of atoms in the condensate state ($p = 0$), N_0/N is given by eq. (7.62). At $T = 0$ K all Bosons are in the condensate. There are no Bosons in excited states, $N_{\text{ex}} = 0$ at $T = 0$ K. This condensation is very similar to the condensation of a gas to a liquid. The atoms in the excited states correspond to the gas, those in the condensate to the liquid.

In a similar way, we could consider a Bose gas at constant temperature T and vary the density. For example, we could fix T (and λ_T) in eq. (7.59) and increase the density n (e.g. reduce V). As n increases (or $v = 1/n = V/N$ decreases), the LHS of eq. (7.59) increases until it reaches a critical value n_c given by

$$n_c \lambda_T^3 = 2.612 \quad (7.63)$$

where again 2.612 is the maximum value of the RHS. For $n > n_c$ we must again include the N_0 Bosons in the $p = 0$ state explicitly so that

$$n = n_c + n_0$$

or

$$\frac{n_0}{n} = \frac{N_0}{N} = 1 - \frac{n_c}{n} = 1 - \frac{v}{v_c}$$

At a given T , the more we compress the gas (increase n or decrease v) the larger the fraction of Bosons that drop into the condensate states. This is an important question for a dilute gas of Bosons in a trap at a given temperature. The higher the density of the gas, the larger the fraction in the condensate. This result is true only if the interparticle interaction is negligible. In an interacting Bose gas the reverse is true because increased density means increased depletion of the condensate by interaction. We now go on to explore the nature of the BEC transition by examining the thermodynamic properties above and below $T_c(n_c)$.

7.3.3 Thermodynamic Properties

In this section we investigate the thermodynamic properties of the ideal Bose gas based on equations (7.55) and (7.56),

$$p = \frac{kT}{\lambda_T^3} g_{5/2}(z) \quad , \quad n = \frac{1}{\lambda_T^3} g_{3/2}(z) \quad (7.64)$$

We show that at and below the critical volume per Boson ($v < v_c$) or critical temperature ($T < T_c$) where BEC takes place, the isothermal compressibility $\kappa_T^{-1} = -V(\partial P/\partial V)_T$ is infinity. This is characteristic of a first order gas to liquid transition in which the gas is condensing into a liquid. In the present case the Bosons are condensing from the excited states to the ground state (BEC) as v is decreased below v_c . We show that there is a latent heat associated with the BEC transition which is also characteristic of a first order transition. This latent heat is consistent with entropy change during BEC. We show when all

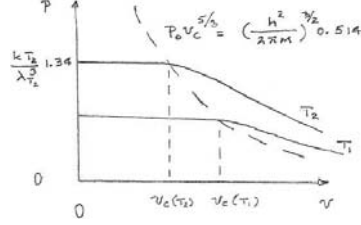


Figure 7.11: Isotherms of the Ideal Bose gas.

the Bosons are in the zero momentum state, the entropy of the gas is zero. The entropy arises entirely from Bosons in the excited states (i.e. from excitations) which is an important concept in understanding superfluidity in interacting Bose fluids and the two fluid model of superfluids. Finally, we evaluate the specific heat below and above T_c .

We first consider $p = (kT/\lambda_T^3) g_{5/2}(z)$ as a function of $v = V/N = n^{-1}$ at constant temperature. At large volume per atom, $v \rightarrow \infty$, the gas becomes classical since the Boson wave functions do not overlap. At $z \rightarrow 0$, z approaches the classical limit, $z = n\lambda_T^3$, and z goes to zero. From the expansion (7.58) $g_{5/2}(z) \rightarrow 0$ as $z \rightarrow 0$. Thus from (7.64) $p \rightarrow 0$ at $v \rightarrow \infty$. As the gas is compressed, z increases, $g_{5/2}(z)$ increases until at $z = 1$, the onset of BEC, $g_{5/2}(z)$ reaches its maximum value, $g_{5/2}(z = 1) = \zeta(5/2) = 1.342$. At $z = 1$ ($v = v_c$) the pressure reaches its maximum value given by

$$p_0 = \frac{kT}{\lambda_T^3} g_{5/2}(1) = \frac{kT}{\lambda_T^3} 1.342. \quad (7.65)$$

The pressure remains at its maximum value p_0 in the Bose condensed phase, $v < v_c$, independent of v . Since p_0 is a constant for $v < v_c$ the gas is infinitely compressible, i.e.

$$\kappa_T^{-1} = -V \left(\frac{\partial p}{\partial V} \right)_T = 0. \quad (7.66)$$

Note that both the equations for p and n in (7.64) include the contributions from excited states only, nothing from the condensate. It is remarkable that as the occupation of the excited states is depleted for $v < v_c$, the pressure remains constant. The variation of $p(v)$ with v at constant temperature is depicted in Fig. 7.11. By eliminating temperature from the equations in (7.64), the pressure and critical volume are found to satisfy the relation,

$$p_0 v_c^{5/3} = \left(\frac{h^2}{2\pi m} \right)^{3/2} \frac{g_{5/2}(1)}{g_{3/2}(1)}. \quad (7.67)$$

Eq. (7.67) for p_0 is plotted in Fig. 7.12 as a function of T . Note that since p_0 is independent of v at the transition we do not need to consider constant v . However, it is useful to consider Fig. 7.12 as a constant v plot at $T > T_c$, on the

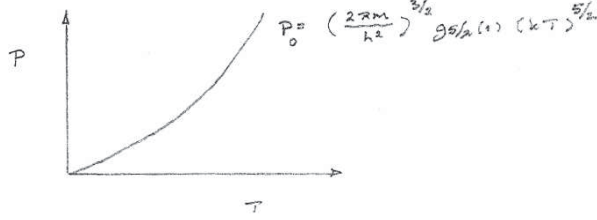


Figure 7.12: The Bose condensed phase pressure versus temperature.

RHS of the transition line. Also, we cannot go to pressures below the transition line. The Bose condensed phase lies on the transition line. From eq. (7.67),

$$\frac{dp_0(T)}{dT} = \frac{5}{2} \frac{kg_{5/2}(1)}{\lambda_T^3} = \frac{1}{Tv_c} \left[\frac{5}{2} kT \frac{g_{5/2}(1)}{g_{3/2}(1)} \right] \quad (7.68)$$

This is the Clapeyron equation $dp_0/dT = \frac{L}{T\Delta v}$ along the transition line, where L is the latent heat of transition and Δv is the volume difference between the two phases. In present case $\Delta v = v_c$ since the specific volume of the condensate (the Bosons in the $p = 0$ state) is zero. The latent heat per Boson is

$$L = \frac{g_{5/2}(1)}{g_{3/2}(1)} \frac{5}{2} kT = R(1) \frac{5}{2} kT = 0.514 \frac{5}{2} kT \quad (7.69)$$

where $R(1) = g_{5/2}(1)/g_{3/2}(1) = 0.514$.

We now discuss the entropy and specific heat of the Bose gas. The internal energy can be obtained as $U = \sum_s n_s \epsilon_s$, and following the same procedure used to evaluate $N = \sum_s n_s$, or by differentiating $\log \mathcal{Z}$ ($U = -\frac{\partial}{\partial \beta} (\log \mathcal{Z})_{z,V}$) to give

$$\frac{U}{N} = \frac{3}{2} \frac{kTv}{\lambda_T^3} g_{5/2}(z). \quad (7.70)$$

The Helmholtz free energy can be obtained from $-\Omega = pV = -(F - \mu N)$ to give

$$\frac{F}{N} = -\frac{kTv}{\lambda_T^3} g_{5/2}(z) + \log z \quad (7.71)$$

from which the entropy is $TS = U - F$ or

$$\frac{S}{N} = \frac{5}{2} \frac{k v}{\lambda_T^3} g_{5/2}(z) - \log z. \quad (7.72)$$

In the Bose condensed phase, the entropy per particle is

$$S = \frac{5}{2} k \frac{v}{\lambda_T^3} g_{5/2}(1) \quad (7.73)$$

which goes to zero at $T = 0$ K. Thus the condensate has zero entropy and all entropy is carried by the excitations (and all U, F , and Ω as well). The specific

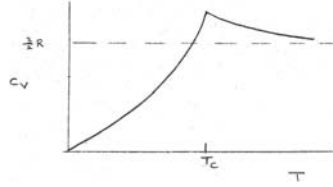
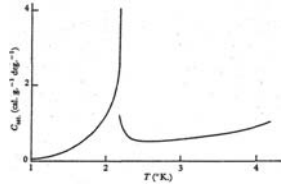


Figure 7.13: The specific heat of a Bose gas.

Figure 7.14: The specific heat of liquid ^4He at the Lambda transition.

heat can be obtained by differentiating U ,

$$\frac{C_V}{N} = \left(\frac{\partial U}{\partial T} \right)_V = \frac{15}{4} \frac{kv}{\lambda_T^3} g_{5/2}(z) - \frac{9}{4} \frac{g_{3/2}(z)}{g_{1/2}(z)}. \quad (7.74)$$

To obtain this result we have to remember the z is a function of T . Using the series expression for $g_\nu(z)$, we find $dg_\nu(z)/dT = (dz/dT)(dg_\nu(z)/dz) = (dz/dT) \frac{1}{z} g_{\nu-1}(z)$. From eq. (7.64) we also have $dg_{3/2}(z)/dT = d(\lambda_T^3 n)/dT = -(\frac{3}{2}T)(\lambda_T^3 n) = -(\frac{3}{2}T) g_{3/2}(z)$. From these two results we obtain $z^{-1}(dz/dT) = -(\frac{3}{2}T) g_{3/2}(z)/g_{1/2}(z)$ and C_V can be obtained by direct differentiation. For $T < T_c$, C_V has only the first term since $g_{5/2}(z=1) = 1.342$ is constant. $C_V(T)$ is shown in Fig. 7.13. In the Bose condensed phase ($T < T_c$) ($z = 1$), $C_V(T)$ is proportional to $T^{3/2}$. The $T^{3/2}$ arises from the density of single particle states $\epsilon_p = p^2/2m$ in the gas which is $g(\epsilon) \propto \epsilon^{1/2}$. In contrast, the density of states for phonon excitations $\epsilon_p = cp$ is $g(\epsilon) \propto \epsilon^2$ which leads to $C_V \propto T^3$ as we saw for phonons in solids and photons. When there is interaction between the Bosons, the excitations become phonon like $\epsilon_p = cp$ at low p and $C_V \propto T^3$. From Fig. 7.13 we see that C_V reaches a peak at T_c and thereafter decreases to the classical limit at high temperature.

The classical limit of the Bose gas is readily obtained by replacing $n\lambda_T^3$ by $g_{3/2}(z)$ in the thermodynamic functions, taking $z \rightarrow 0$ and $g_\nu(z) \sim z$ at $z \rightarrow 0$. Eq. (7.61) reduces to

$$p = \frac{kT}{\lambda_T^3} g_{5/2}(z) = kTn \frac{g_{5/2}(z)}{g_{3/2}(z)} \rightarrow \frac{kTN}{V} \quad (7.75)$$

which is the classical ideal gas law. Similarly,

$$U = \frac{3}{2}kTV g_{5/2}(z) = \frac{3}{2}NkT \frac{g_{5/2}(z)}{g_{3/2}(z)} \rightarrow \frac{3}{2}NkT \quad (7.76)$$

which is the classical gas translational kinetic energy.