PY3104 Statistical Thermodynamics

Calum Ross[1]
Last Updated March 29, 2021

Contents

---

[1]calumross[at]ucc.ie

1 Introduction

These rough lecture notes for PY3104 Statistical Thermodynamics. The course consists of 24 lectures and is based on [Man71, Gue07, KK80] with some extra content from [SS75, AM20]. From [Man71] we will use Chapters 6, 7, 9, 11, and 12 (in first edition this is separate in the second edition this is merged with chapter 11). Sections with a ∗ next to them were not lectured and are included for completeness. Another nice reference that is a bit more conversational is [Atk07], this discusses classical thermodynamics with a chapter focused on each law. The first part of the course is base on existing lecture notes written by Andy Ruth.

The aim of the course is to give an understanding of how to describe equilibrium and non-equilibrium states of matter. Calculating macroscopic (thermodynamic) quantities from microscopic (quantum mechanics/ spectroscopic) properties of matter. There are two strands to thermodynamics

1. Phenomenological theories: Described in terms of classical concepts such as pressure, temperature, and volume. They result in relative changes of variables.

2. Statistical theories: Utilise quantum mechanical concepts such as dispersion relations, particle statistics, etc. These yield absolute values of variables based on time averages/ expectation values.

Some of the key concepts that we will need through out the course include:

- Macrostate: The thermodynamic state of a system. e.g. specification of a system by thermodynamic properties/ coordinates P, V, B, M, surface tension, surface area, particle number (N), etc. A macrostate is labelled by these variables e.g. (N, U, V) or (N, P, T).

- Microstate: Most detailed specification of the assembly. e.g. in classical kinetic theory of gases it involves specifying the position and momentum of each of the N particles. Many

microstates can be consistent with a given macrostate. There is a very large but finite number of such microstates, called Ω. To give an idea of the size $\Omega \sim N^N$.

- Distributions: These give an in between picture where we do not keep track of the microstates but just at how the particles are distributed by energy for example. There are two useful definitions of a distribution:

  1. In states: $(n_1, n_2, n_3, \ldots, n_j, \ldots) = \{n_j\}$ where n_j = number of particles in state j with energy energy ϵ_j.

  2. In levels: $(n_1, n_2, n_3, \ldots, n_i, \ldots) = \{n_i\}$ where n_i = number of particles in level i. Here level i means the states with energy ε_i and degeneracy g_i.

  $t(\{n_j\})$ = number of microstates consistent with $\{n_j\}$, is called the statistical weight of the distribution.

Finally it is useful to state here the laws of thermodynamics that will be useful throughout this course.

Zeroth Law: Existence of thermodynamic equilibrium.

1st Law: Energy is conserved.

2nd Law: Heat flows spontaneously from high to low temperature.

3rd Law: Entropy is constant at $T = 0$.

In different contexts people will attribute other laws as laws of thermodynamics. For the most part these are very context dependent and we will not be concerned with them here.

2 State Variables, the First and Second Law

2.1 State Variables

This section is mostly a revision of the second year course PY2104: Introduction to Thermodynamics and Statistical Physics.

An important basic concept is that of an equilibrium state, sometimes called a thermal state. This is a state in which all past history is forgotten and all macroscopic quantities cease to change in time. e.g. $\frac{dT}{dt} = 0$. *There is no macroscopic flow present.* This is similar to the condition in classical mechanics that equilibrium is when there are no net forces acting on the system.

Non-equilibrium states then correspond to states where macroscopic quantities depend on time and space; e.g. heat conduction due to a temperature gradient, diffusion due to a concentration gradient, electric current, excitation and relaxation processes after laser excitation, etc.

The 0th law of thermodynamics is taken to be the axiom: *After a sufficiently long time all thermodynamic systems will reach a state of equilibrium.* In other words there is a spontaneous tendency of a system to reach an equilibrium state where macroscopic quantities stop evolving in time.

The thermodynamic state of a system consisting of many particles (say 10^{23}) can be completely specified in terms of a few, usually two or three, independent state variables, using appropriate equations of state. e.g. The ideal gas law, the Van der Waals equation, thermal expansion of solids, etc. These variables come in two varieties:

- Extensive state variables: Proportional to the size of the system.

- Intensive state variables: Independent of the size of the system.

Here the size of the system means both the spatial extent and the amount of matter in the system. Examples of these state variables are included in Table. 1

Certain pairs of state variables often occur together as a product. This is because they correspond to generalised forces and generalised displacements, and their product gives a kind of energy. Some appear in expressions for mechanical work, and others in expressions for heat and chemical work.

Schematically the relation is *Internal energy = Mechanical work & Heat & Chemical work*. The split of variables between the different types of energy is given in Table. 1. The thermodynamic potentials which are expressed in terms of products of state variables are give in Table. 2.

Extensive	Intensive
Mechanical Work Related	
Volume, V	Pressure, $-P$
Magnetization, M	Magnetic Field, H
Polarization, $\mathcal{P}$	Electric Field, $\mathcal{E}$
Area, A	Surface Tension, σ
Quantity, X (displacement)	Quantity, Y (force)
Heat Related	
Entropy, S	Temperature, T
Chemical Work Related	
Number of Particles, N	Chemical Potential, μ

Table 1: Examples of Extensive and intensive variables along with the "type of" energy they are related to. The minus sign in the pressure is important.

Caloric (Thermal Potentials)
Internal Energy, U
Enthalpy, H
Helmholtz (Free) Energy , F
Gibbs (Free) Enthalpy , G
Grand Potential , J

Table 2: Thermodynamic potentials, some of the crucial objects in study of thermodynamics

There are also response functions, which measure how a material reacts to certain stimuli:

- Thermal: Heat capacities for response to applying heat, ...

- Mechanical: Compressibility, Susceptibility e.g. magnetic and electric, ...

If a system is changed from one equilibrium state, S_1, to another, S_2, then the amount by which the state variables change are independent of the chose process, the path taken through "*Phase space*". The energy form, however, depends on the process involved. Hence changes in state variables correspond to *Exact Differentials*!

Definition 2.1. *A function $F(x_1, x_2)$ of at least two independent variables, x_1, x_2 has differential*

$$dF = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} dx_1 + \left(\frac{\partial F}{\partial x_2}\right)_{x_1} dx_2, \tag{2.1}$$

where $\left(\frac{\partial F}{\partial x_1}\right)_{x_2}$ means the derivative of F with respect to x_1 holding x_2 constant. If F and its derivative are continuous and

$$\left(\frac{\partial}{\partial x_1}\left(\frac{\partial F}{\partial x_2}\right)_{x_1}\right)_{x_2} = \left(\frac{\partial}{\partial x_2}\left(\frac{\partial F}{\partial x_1}\right)_{x_2}\right)_{x_1} \tag{2.2}$$

e.g. the partial derivatives commute, then dF is called an exact differential.

Letting $c_1(x_1, x_2) = \left(\frac{\partial F}{\partial x_1}\right)_{x_2}, c_2(x_1, x_2) = \left(\frac{\partial F}{\partial x_2}\right)_{x_1}$ it is straight forward to see that a function having an exact differential is equivalent to it having the following properties:

(a) The integral of dF depends only on the end points not the path taken,

$$F(B) - F(A) = \int_A^B dF = \int_A^B (c_1 dx_1 + c_2 dx_2). \tag{2.3}$$

(b) For a closed path the integral of dF vanishes, this follows from the above result about path independence,

$$\oint dF = \oint (c_1 dx_1 + c_2 dx_2) = 0. \tag{2.4}$$

(c) By integrating dF the function F can be found up to an additive constant.

Exact differentials may be familiar from mechanics or vector calculus where conservative forces are defined to be the gradient of a potential function. Any function that can be expressed as a gradient also satisfies the above properties of path independence.

2.2 First Law of Thermodynamics

The First Law of
Thermodynamics:
Heat is work and work is heat.
Heat is work and work is heat.
Very good!

*Thermodynamics by Flanders
and Swann*

The first law of thermodynamics is often stated as *Energy is conserved*. In any system there is a "store" of energy called the internal energy, labelled U. The internal energy can be changed in the following way:

- Causing the system to do mechanical work.

- Adding heat, dQ, to the system.

- Adding matter to the system, μdN mechanical work.

As energy is conserved dU is an exact differential given by

$$dU = dQ - dW + \mu dN. \tag{2.5}$$

The sign in front of W is due to the convention of work being done by the system reducing its energy, this also explains why there is a minus sign in front of P in Table. 1. The mechanical work is given by

$$dW = PdV - \sigma dA - \mathcal{E}d\mathcal{P} - \mathcal{H}dM, \tag{2.6}$$

in this relation $\mathcal{E}$ is pared with $\mathcal{P}$ and $\mathcal{H}$ with M because the polarisation and magnetisation of a system determine how it responds to an external electric and magnetic field.

It turns out that while dV, dA, dP, dM, and dN are exact differentials the heat (dQ) and the mechanical work are not exact!. They depend on the path, this means that W and Q are <u>not</u> state variables. To signify this they are sometimes written as $đQ$ and $đW$.

Example 2.2. A good example to have in mind comes from classical mechanics in $1D$. The work is given in terms of the force as $dW = \pm F dx$, where the exact sign depends on the conventions for work done. This is exact when the Force is just a function of x, in other words when the force is conservative and the work is related to the potential energy of a system. There are many forces which are not conservative, thus the work done due to them is not an exact differential.

For a system with multiple constituents, e.g. types of particle, Equation. (2.5) generalises to

$$dU = dQ - YdX + \sum_i \mu_i dN_i \tag{2.7}$$

where i runs over the constituents. If we were considering Air which is a mixture of different atomic gases then i would run over the different gases N_2, O_2, Ar, CO_2

6

2.3 Second Law of Thermodynamics

The Second Law of
Thermodynamics: Heat won't
pass from a cooler to a hotter.
You can try it if you like but you
far better notter. 'Cos the cold
in the cooler with get hotter as
a ruler. 'Cos the hotter body's
heat will pass to the cooler

Thermodynamics by Flanders
and Swann

The second law of thermodynamics can be summarised as *Heat flows spontaneously from high temperatures to low temperatures.* The state variable entropy, S, is a measure of the disorder in a system, it is intimately linked with the second law of thermodynamics. Another way to state the second law is that for any system undergoing any process the entropy change, dS, of the system and its surroundings is positive, and approaches zero for a reversible process.

Definition 2.3. *A Phenomenological definition of the entropy for a reversible process is*

$$dS = \frac{dQ}{T}. \tag{2.8}$$

Using this definition the second law can then be written as

$$dS \geq \frac{dQ}{T}. \tag{2.9}$$

Changes in the entropy are related to changes in the extensive state variables U, V, N through the combination of the first and second laws: the first law states $dU = dQ - dW + \mu dN$ which can be re written as

$$dQ = dU + dW - \mu dN, \tag{2.10}$$

leading to a rewriting of the second law as

$$TdS \geq dQ = dU + PdV - \mu dN. \tag{2.11}$$

Note that the independent natural state variables of the entropy are U, V and N. In other words they lead to the fundamental definition of other state variables.

As the entropy $S(U, V, N)$ is a state variable, its differential is exact:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{V,U} dN. \tag{2.12}$$

For an equilibrium (reversible) process the inequality in Equation. (2.11) is saturates:

$$dS = \frac{dQ}{T} = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN. \tag{2.13}$$

Thus we find that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}, \tag{2.14}$$

$$P = T\left(\frac{\partial S}{\partial V}\right)_{U,N}, \tag{2.15}$$

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{V,U}. \tag{2.16}$$

It is common to take Equation.(2.14) as a definition of temperature, and Equation. (2.16) is the first of many potential definitions of the chemical potential that we will meet.

The entropy of a system is an extensive, additive state variable. This means that if our system consists of several independent subsystems the entropy of the total system is the sum of the subsystem entropies. This is a very useful property, and it is very common to consider the combination of two subsystems when working with thermodynamic concepts. This is shown in Figure. 1
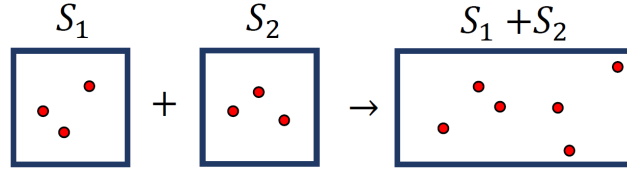

Figure 1: A schematic of the addition of the entropy for isolated systems.

As a mathematical exercise we can introduce a scale factor into the entropy, $\lambda S(U, V, N) = S(\lambda U, \lambda V, \lambda N)$. Differentiating this relation gives

$$\begin{aligned}
S &= \frac{d\lambda S}{d\lambda}, \\
&= \left(\frac{\partial S}{\partial \lambda U}\right)_{V,N} \frac{d\lambda U}{d\lambda} + \left(\frac{\partial S}{\partial \lambda V}\right)_{U,N} \frac{d\lambda V}{d\lambda} + \left(\frac{\partial S}{\partial \lambda N}\right)_{V,U} \frac{d\lambda N}{d\lambda}, \\
&= \left(\frac{\partial S}{\partial \lambda U}\right)_{V,N} U + \left(\frac{\partial S}{\partial \lambda V}\right)_{U,N} V + \left(\frac{\partial S}{\partial \lambda N}\right)_{V,U} N.
\end{aligned} \tag{2.17}$$

At $\lambda = 1$ this becomes

$$S = \frac{U}{T} + \frac{PV}{T} - \frac{\mu N}{T}, \tag{2.18}$$

which rearranges to give

$$U = TS - PV + \mu N. \tag{2.19}$$

Equation. (2.19) is known as the Euler relation, sometimes Euler equation, and is useful for deriving other thermodynamic relations.

2.4 Thermodynamic Potentials

A state variable is called a thermodynamic potential with respect to a complete set of state variables, if knowledge of the state variables is sufficient to determine all other state variables. The entropy $S(U, V, N)$ is one example of a thermodynamic potential. It is a particularly important one as it governs equilibrium conditions. Many thermodynamic potentials, the related state variables, and their Euler relations are summarised in Table. 3 at the end of this section.

Consider the internal energy $U(S, V, N)$ as a state variable. Its differential is exact:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{V,S} dN, \tag{2.20}$$

comparison of this with the first law from Equation. (2.5) ($dU = TdS - PdV + \mu dN$) we find

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}, \tag{2.21}$$

$$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N}, \tag{2.22}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{V,S}. \tag{2.23}$$

The third relation, Equation. (2.23), gives another way to define the chemical potential.

From the above relations we see that the temperature governs the flow of energy, while the chemical potential governs the flow of mass.

The two thermodynamic potentials $S(U, V, N)$ and $U(S, V, N)$ are not particularly practical since entropy cannot be directly measured in experiments. Temperature is an easier quantity to measure and control. Thus it is be better to use T, V, N as the independent variables. The *Helmholtz free energy*, $F(T, V, N)$ is the relevant thermodynamic potential in this case. It is related to the internal energy through the Legendre transform[2]

$$F = U - TS. \tag{2.24}$$

---

[2]Legendre transforms may be familiar to some of you from classical mechanics where they relate the Lagrangian and Hamiltonian interpretations. The occurrence of Legendre transforms in both classical mechanics and thermodynamics hints at a relationship between the two subjects. We will not discuss this here but there are a very nice series of blog posts by John Baez discussing this, see Classical Mechanics versus Thermodynamics for the first post.

This implies that $dF = dU - TdS - SdT$ which combines with the first law, expressed through Equation. (2.5), to give

$$dF = -SdT - PdV + \mu dN. \tag{2.25}$$

Again we make use of this being an exact differential to compare with

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{V,T} dN. \tag{2.26}$$

This comparison yields the relations

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N}, \tag{2.27}$$

$$-P = \left(\frac{\partial F}{\partial V}\right)_{T,N}, \tag{2.28}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}, \tag{2.29}$$

where again we find a new way of expressing the chemical potential, as you can probably guess we will find one for every thermodynamic potential which is expressed as a function of the number of particles[3] N.

Example 2.4. As a brief aside we can use the relationship between P and F to get an interpretation of pressure as split into energy and entropy related pieces. This is demonstrated in the following way,

$$\begin{aligned}
P &= -\left(\frac{\partial F}{\partial V}\right)_{T,N} \\
&= -\left(\frac{\partial U}{\partial V} - T\frac{\partial S}{\partial V} - S\frac{\partial T}{\partial V}\right)_{T,N} \\
&= -\left(\frac{\partial U}{\partial V} - T\frac{\partial S}{\partial V}\right)_{T,N} \\
&= -\left(\frac{\partial U}{\partial V}\right)_{T,N} + \left(T\frac{\partial S}{\partial V}\right)_{T,N},
\end{aligned}$$

where the first term on the last line is the energy pressure which is dominant in solids, and the second term is the entropy pressure which is dominant in gases. Going between the second and third line the derivative of T disappears as the differentiation is being carried out at constant T.

As we have seen in the three cases above, thermal state variables are derived from the thermodynamic potentials. By considering derivatives of thermal state variables such as P, V, T, and

---

[3]This is an example of a deep underlying principal, that N and μ are canonically conjugate variables. This is true for all of the pairs of state variables that appear together in thermodynamic potentials: they are conjugate variables; one is a generalised position and the other is a generalised force. Again this formalism hints at a familiar picture from the Hamiltonian picture of classical mechanics.

S we get relationships between them. These relationships are called Maxwell relations, they follow from the fact that the thermodynamic potentials have exact differentials.

Examples of Maxwell relations are included in the problems for the course.

Alongside temperature, pressure is a quantity which is easy to measure and control. Considering (T, P, N) as the independent variables leads to a fourth thermodynamic potential, the *Gibbs free enthalpy*

$$G(T, P, N) = F + PV = U - TS + PV. \tag{2.30}$$

Its differential is

$$dG = dF + PdV + VdP = dU - TdS - SdT + PdV + VdP, \tag{2.31}$$

as will be familiar by now we use Equation. (2.5) to re express it as

$$dG = -SdT + VdP + \mu dN. \tag{2.32}$$

Next we compare with the exact differential

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{P,T} dN \tag{2.33}$$

to find the relations

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N}, \tag{2.34}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}, \tag{2.35}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}. \tag{2.36}$$

Finally if we consider the independent state variables (S, P, N) the *enthalpy* is the relevant thermodynamic potential

$$H(S, P, N) = U + PV. \tag{2.37}$$

Its differential can be written as

$$dH = dU + PdV + VdP = TdS + VdP + \mu dN. \tag{2.38}$$

The differential being exact leads to

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}, \tag{2.39}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,N}, \tag{2.40}$$

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}. \tag{2.41}$$
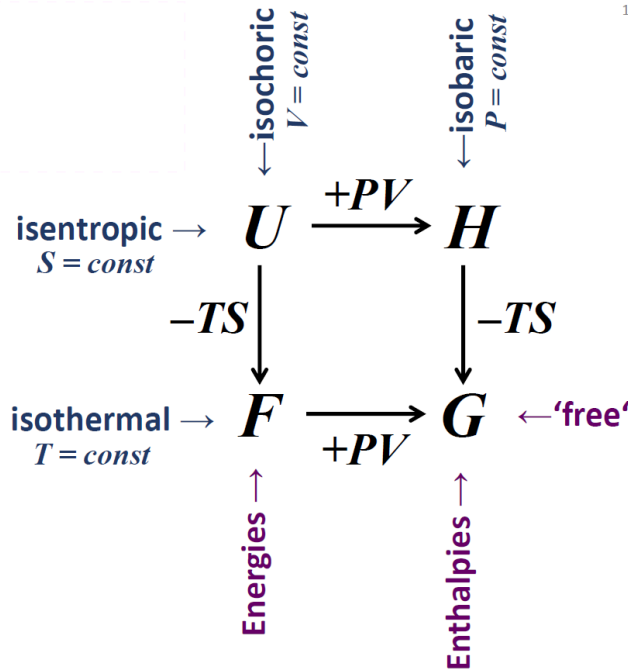
Figure 2: A square summarising the Legendre transformations relating four of the most commoly used thermodynamic potentials.

The relationship between the internal energy, enthalpy, Helmholtz free energy, and Gibbs free enthalpy are nicely summarised in Figure. 2

These thermodynamic potentials are all related through Legendre transformations for a closed system, i.e the particle number N is a constant. As shown in Table. 3 there are thermodynamic potentials, such as the grand canonical potential J, which describe open systems where N is allowed to change.

Another convenient way to keep track of the thermodynamic potentials and their relationships is through the diagram in Figure. 3

Figure 3: The natural state variables on are on either side of the relevant thermodynamic potential. The partial derivative of the potential with respect to a natural variable results in the opposite natural variable, going against the arrow results in a minus sign.

In Table 3 the first four thermodynamic potentials are suited for an isolated system, where

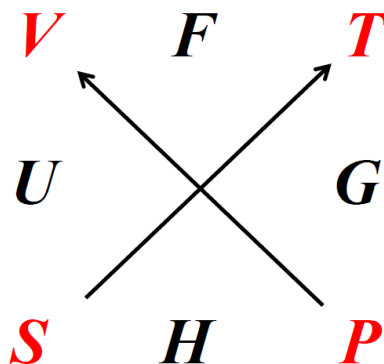| State Variables	Thermodynamic Potentials	Euler Relations	Gibbs Equations
S, V, N	U	$U = TS - PV + \mu N$	$dU = TdS - PdV + \mu dN$
S, P, N	$H = U + PV$	$H = TS + \mu N$	$dH = TdS + VdP + \mu dN$
T, V, N	$F = U - TS$	$F = -PV + \mu N$	$dF = -SdT - PdV + \mu dN$
T, P, N	$G = U - TS + PV$	$G = \mu N$	$dG = -SdT + VdP + \mu dN$
U, V, N	S	$S = \frac{U}{T} + \frac{PV}{T} - \frac{\mu N}{T}$	$dS = \frac{dU}{T} + \frac{PdV}{T} - \frac{\mu dN}{T}$
$\frac{1}{T}, V, N$	$\Phi = S - \frac{U}{T}$	$\Phi = \frac{PV}{T} - \frac{\mu N}{T}$	$d\Phi = -Ud\left(\frac{1}{T}\right) + \frac{PdV}{T} - \frac{\mu dN}{T}$
$U, \frac{P}{T}, N$	$\Psi = S - \frac{PV}{T}$	$\Psi = \frac{U}{T} - \frac{\mu N}{T}$	$d\Psi = \frac{dU}{T} - Vd\left(\frac{P}{T}\right) - \frac{\mu dN}{T}$
$\frac{1}{T}, \frac{P}{T}, N$	$\Upsilon = S - \frac{U}{T} - \frac{PV}{T}$	$\Upsilon = -\frac{\mu N}{T}$	$d\Upsilon = -Ud\left(\frac{1}{T}\right) - Vd\left(\frac{P}{T}\right) - \frac{\mu dN}{T}$
S, V, μ	$I = U - \mu N$	$I = TS - PV$	$dI = TdS - PdV - Nd\mu$
T, V, μ	$J = U - TS - \mu N$	$J = -PV$	$dJ = -SdT - PdV - Nd\mu$
S, P, μ	$K = U + PV - \mu N$	$K = TS$	$dK = TdS + VdP - Nd\mu$
T, P, μ	$L = U - TS + PV - \mu N$	$L = 0$	$dL = -SdT + VdP - Nd\mu = 0$

Table 3: A table summarising all of the Thermodynamic potentials, state variables, and their relationships. When μ becomes a state variable we are considering systems where the particle number N can change. J is called the grand canonical potential.

energy and mass do not mix between the system and its surroundings. The next four are best suited to closed system, heat is transferred between a system and its surroundings but matter is not. The final four are adapted to open systems, where mass and energy is transferred between the system and the surroundings. Later in the course we will encounter different thermodynamic ensembles corresponding to the case of isolated, closed, and open systems.

3 Systems in Thermodynamic Equilibrium

> The zeroth law implies the existence of a criterion of thermal equilibrium.
>
> *Four Laws that Drive the*
> *Universe by Peter Atkins*

3.1 Equilibrium Conditions

Equilibrium is characterised through the behaviour of the entropy and the second law. This is because irreversible processes cause the entropy to increase, $dS > 0$. Upon reaching equilibrium[4] there are only equilibrium processes, the entropy then attains a maximum value $S = S_{max}$ and is no longer changing[5], $dS = 0$. This is the maximum value subject to some constraints on

---

[4]Remember, equilibrium is a dynamical process. While the macroscopic state variables are not changing in time the system is not static. For example, in diffusive equilibrium particles are still moving between the two parts of the system. However, the chemical potential has been equalised between the two parts of the system.

[5]This is the entropy of the total process including the system and its surroundings. The individual reversible processes can lead to small changes in entropy, which are balanced by entropy changes in other parts of the

the state variables, referred to as *side conditions*, determined by the system and experimental conditions.

To define equilibrium we need to find this extreme value subject to the side conditions. One way to do this is to use the variational principle; consider a thermodynamic potential $S(U, V, N)$ and infinitesimally change the state variables $U, V, N \rightarrow U + \delta U, V + \delta V, N + \delta N$. If the thermodynamic takes an extremal value, a maximum or minimum, then we want it to be invariant under these changes, e.g $\delta S = 0$. In other words at equilibrium the Thermodynamic potential is invariant with respect to the variation of state variables. Imposing this condition leads to relationships between thermodynamic variables, the equilibrium conditions!

In our example

$$\delta S = \left(\frac{\partial S}{\partial U} \right) \delta U + \left(\frac{\partial S}{\partial V} \right) \delta V + \left(\frac{\partial S}{\partial N} \right) \delta N, \tag{3.1}$$

and the equilibrium conditions are

$$\frac{\partial S}{\partial U} = 0, \tag{3.2}$$

$$\frac{\partial S}{\partial V} = 0, \tag{3.3}$$

$$\frac{\partial S}{\partial N} = 0. \tag{3.4}$$

It is important to remember that this is the total entropy! It is split up into pieces for the surroundings and every component of the system.

More generally for the entropy the equilibrium condition is $\delta S = 0$, S is an extremal values, and $\delta^2 S < 0$, it is a maximum.

Depending on the system different Thermodynamic potentials will be best suited to describing equilibrium. To find the conditions for the other potentials we use the first and second laws of thermodynamics and consider a variation in the heat with N held constant:

- $\delta Q = dU + PdV$ so $dU \leq TdS - PdV$,

- $\delta Q = dH - VdP$ so $dU \leq TdS + VdP$,

- $\delta Q = dF + TdS + SdT + PdV$ so $dF \leq -SdT - PdV$,

- $\delta Q = dG + TdS + SdT - VdP$ so $dG \leq -SdT + VdP$.

These are not universal conditions as they depend on the side conditions. Extremising the thermodynamic potentials, in the manner outlined above leads to the equilibrium conditions:

- $\delta U = 0$, S and $\delta^2 U > 0$, U is minimised,

- $\delta H = 0$, S and $\delta^2 H > 0$, H is minimised,

- $\delta F = 0$, S and $\delta^2 F > 0$, F is minimised,

- $\delta G = 0$, S and $\delta^2 G > 0$, G is minimised.

process and in the environment.

3.1.1 Examples

Example 3.1. Flow of energy
Consider a gas in a box, split into two pieces separated by a rigid, perfectly insulating dividing wall. In the insulated system the two compartments have different internal energies, volumes, and particle numbers. The difference in internal energy results in the two compartments having a different temperature. For the total system the state variables are the sum of those of the components; $U = U_1 + U_2$, $V = V_1 + V_2$, and $N = N_1 + N_2$. This is an isolated system so N, V, U are all constant for the whole system.
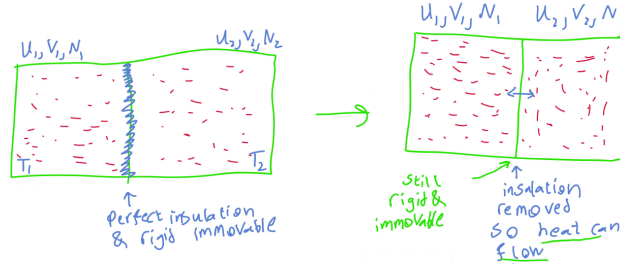

Figure 4: A system consists of two boxes initially separated by a perfectly rigid insulating wall. If the insulation is removed the wall will conduct heat until the equilibrium is reached

The thermodynamic potential to work with is the entropy, $S(U, V, N)$. The compartments exchange heat, dQ until the system reaches equilibrium.

The rigid solid walls imply that $dV_i = 0 = dN_i$. The equilibrium condition is that $S = S_{max}$. The internal energy of the compartments change due to the exchange of heat.

$$U_2 = U - U_1, \qquad \delta U_2 = -\delta U_1. \tag{3.5}$$

This implies that

$$\delta S = \left(\frac{\partial S}{\partial U_1}\right)\delta U_1 + \left(\frac{\partial S}{\partial U_2}\right)\delta U_2 \tag{3.6}$$

$$= \left(\frac{\partial S}{\partial U_1} - \frac{\partial S}{\partial U_2}\right)\delta U_1 \tag{3.7}$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta U_1, \tag{3.8}$$

this vanishes when the temperatures agree $T_1 = T_2$. This is called the condition for thermal equilibrium.

Example 3.2. Flow of matter
Consider gas in two boxes sitting in a temperature bath. The boxes are connected by a pipe with a valve in it. When the valve is open particles can move between the two boxes. The boxes can both exchange heat with the reservoir and we will assume that they are in thermal equilibrium.

Initially the valve is closed and $N_1 \neq N_2, \mu_1 \neq \mu_2$. For the total system we have that $T =$
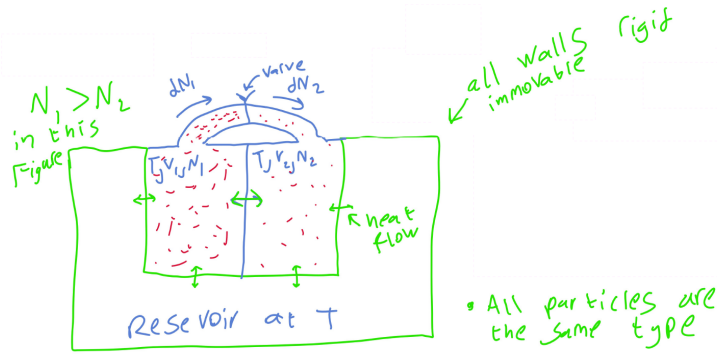
Figure 5: A system consists of two boxes in thermal equilibrium. A pipe connects the boxes that particles can flow through.

constant, $V = V_1 + V_2$, and $N = N_1 + N_2$. When the valve is open the boxes will exchange particles until they are in equilibrium, in this case diffusive equilibrium.

$$0 = dN = dN_1 + dN_2 \quad \Rightarrow dN_1 = -dN_2. \tag{3.9}$$

Contact with the reservoir and the rigidity of the walls imply that $dT = 0 = dV_i$.

The easiest thermodynamic potential to work with is the Helmholtz free energy, $F(T, V, N)$. Equilibrium is when F is minimised subject to changes in the particle numbers. This implies that

$$(\delta F)_{T,V,N} = \left(\frac{\partial F}{\partial N_1}\right)_{T,V} \delta N_1 + \left(\frac{\partial F}{\partial N_2}\right)_{T,V} \delta N_2 \tag{3.10}$$

$$= \left[\left(\frac{\partial F}{\partial N_1}\right)_{T,V} - \left(\frac{\partial F}{\partial N_2}\right)_{T,V}\right] \delta N_1 \tag{3.11}$$

$$= [\mu_1 - \mu_2] \, \delta N_1, \tag{3.12}$$

this vanishes when the diffusive equilibrium condition is satisfied, $\mu_1 = \mu_2$.

You will consider mechanical equilibrium on the first problem sheet.

From the examples and the problem sheet we see that: Temperature controls the flow of energy; μ governs the flow of mass; and pressure governs the "flow" of work. Systems are in both thermodynamic and diffusive equilibrium if $\mu_1 = \mu_2$ and $T_1 = T_2$.

3.2 Chemical Potential and Gibbs Enthalpy

The Gibbs free enthalpy is closely related to the chemical potential. The Euler relation $U = TS - PV + \mu N$ leads to

$$\mu = \frac{G}{N}. \tag{3.13}$$

This expression gives the intuition that the chemical potential is some sort of "energy" per particle.

In the presence of a potential difference there will be another contribution to the chemical potential, called the external chemical potential.

More to follow

4 Statistical Thermodynamics

> The aim of statistical thermodynamics is to make a bridge between the over-elaborate detail of mechanics and the obscure generalities of thermodynamics.
>
> ―――――――――――――――
> *Statistical Physics by Tony Genault*

4.1 Basics

Thermodynamic entities, or particles, can be: atoms, molecules, electrons, photons, oscillators, etc. Generally we assume that a single type of particles and that there are N identical, or indistinguishable, particles. These N particles constitute a system, also called an assembly. A collection of assemblies, all constructed in the same way, is called an *ensemble*.

The energy of every entity is quantised. From the distribution of entities in the system among its quantum states, e.g atomic orbitals. Macroscopic properties, state variables, are determined from expectation values of this distribution.

The key definitions that we saw in the introduction are

- Microstate: specified by the number of particles in individual quantum states. These states can be degenerate, have the same energy, and the "extra" states are counted.

- Macrostate (system configuration): A state of the system where the distribution of particles over individual quantum states is specified. e.g. number of particles in each quantum state is specified.

- Thermodynamic probability (w_k): Number of microstates in a macrostate k. Strictly speaking this is not a probability as it has not been normalised, this is done by dividing by the total number of microstates.

- Statistical weight (multiplicity): Number of microstates in a system, $\Omega = \sum_k w_k$.

Generally the statistical weight is a function of the state variables, $\Omega(U, V, N)$.

4.2 Binary Model

We now turn to our first example of a statistical mode; a binary system for a particle with spin. Consider an electron in the ground state of a hydrogen atom. This electron has either

spin up or spin down, there is a binary choice for its spin. This electron is like a coin with spin up corresponding to heads and spin down corresponding to tails.

A natural question is, how many ways are there for N spins to be arranged? In other words for a gas with N hydrogen atoms, how many arrangements are there for the electrons? Another way to phrase this is to ask how many configurations are there with k spin ups.

Saying that a configuration has k spin ups is specifying the macrostate, a microstate corresponds to specifying the spin of all N electrons with k of those having spin up. Thus every microstate with k spin ups corresponds to the same macrostate.

Example 4.1. Binary System
Let us consider the possible microstates for N atoms when N is small. This is shown in Figure 6
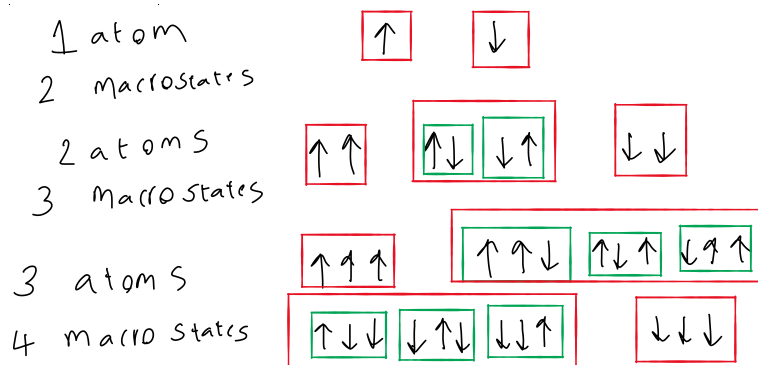
Figure 6: Microstates and macro states for binary spin system with $N = 1, 2, 3$ atoms.

The number of microstates in a macrostate follows the pattern of Pascal's triangle as shown in Figure 7. The averaging postulate, or the principle of statistical inevitability, says that the most probably macrostate is the one consistent with the largest number of microstates.

$N = 0$							1						
$N = 1$						1		1					
$N = 2$					1		2		1				
$N = 3$				1		3		3		1			
$N = 4$			1		4		6		4		1		
$N = 5$		1		5		10		10		5		1	
$N = 6$	1		6		15		20		15		6		1

Figure 7: The number of microstates in a given macrostate for an N-particle binary system follows Pascal's triangle.

The numbers in Pascal's triangle correspond to the coefficients in the binomial expansion,

$$(x + y)^N = \sum_{k=0}^{N} \frac{N!}{(N-k)!k!} x^{N-k} y^k. \tag{4.1}$$

In this expression we can think of x as being $\uparrow$ for spin or heads for the coin, and y as being $\downarrow$ for spin or tails for the coin. As some more notation, $k = N_\uparrow$ is the number of $\uparrow$ spins in the macrostate, and $N - k = N_\downarrow$ is the number of $\downarrow$ spins in the macrostate.

From Equation (4.1) we can read off that the thermodynamic probabilities and Ω:

$$w_k(N) = \frac{N!}{(N-k)!k!}, \tag{4.2}$$

$$\Omega = \sum_{k=0}^{N} w_k(N) = 2^N. \tag{4.3}$$

The statistical weight is extremely large for a large collection of spins. For example for $N = 50$ $\Omega \simeq 10^{14}$ and for a mole of spins $\Omega \simeq 2^{10^{23}}$.

The general approach is to find $w_k(N)$ as a function of k for a given large N. The principal of statistical inevitability [6] then says that the macrostate with the largest number of microstates is the most probable and determines the macroscopic properties of the system. e.g. it is the equilibrium state. The sum over $w_k(N)$ then yields the statistical weight.

Include an example figure here.

4.3 Harmonic Oscillator

Our next example is to consider a system of harmonic oscillators, e.g. atoms in a crystal lattice[7]. From the Schrödinger equation we know that the eigenfunctions for the harmonic oscillator are the non-degenerate Hermite polynomials with eigenvalues

$$\varepsilon_n = \left(n + \frac{1}{2}\right) h\nu = n\varepsilon + \frac{h\nu}{2}. \tag{4.4}$$

The integer n is called the quantum number and determines the energy level. Here we will redefine the energy so that it starts at 0 for $n = 0$, $\varepsilon_n \to \varepsilon_n - \frac{h\nu}{2}$. Here we will assume that there are three oscillators, $N = 3$, but everything works for general N. We also assume the system is at temperature T with total energy $E = 3\varepsilon$, this is the energy available to the system above the zero point energy. A natural question is: How can the energy be distributed among the states?

(1) If the oscillators are distinguishable:

---

[6] Also known as the averaging postulate.

[7] It is only in the first order approximation that we can think of a crystal as a series of uncoupled oscillators, there will be corrections to this coming from coupling between atoms. However, the first order approximation can get us surprisingly far
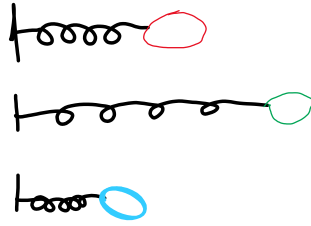
Figure 8: Three distinguishable harmonic oscillators.

    (a) Oscillators are allowed to occupy the same states.

(2) If the oscillators are indistinguishable:

    (a) Oscillators are allowed to occupy the same states.

    (b) Oscillators are not allowed to occupy the same states.

We will encounter type (2) in detail when we talk about Bosons and Fermions. First focus on type (1), distinguishable oscillators. The energy spectrum of an oscillator is given in Figure 9.
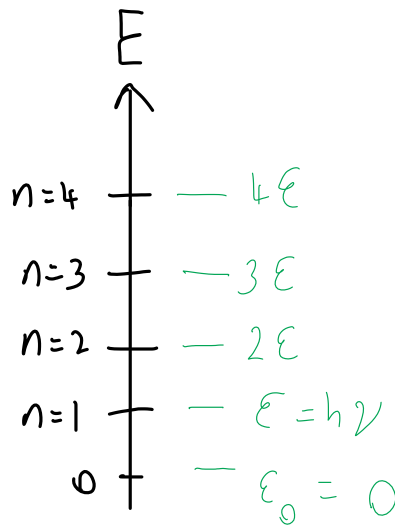
Figure 9: The energy spectrum of a quantum mechanical harmonic oscillator.

We call the number of oscillators with energy ε_i the *occupation number* of the i'th energy level and denote it n_i. The sum of the occupation numbers is the total particle number, $N = \sum_j n_j = 3$ and the total energy is $E = \sum_j n_j \varepsilon_j = 3\varepsilon$. The macrostates are labelled by the occupation number of the zero'th energy level, $k = n_0$. The microstates and macrostates are shown in Figure 10
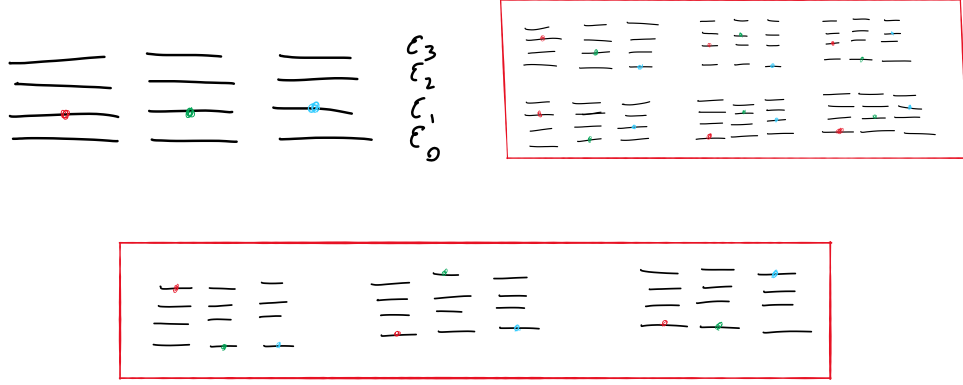
Figure 10: The micro states of the 3-oscillator system. On the top left the microstate has $n_0 = 0, n_1 = 3, n_2 = 0, n_3 = 0$ and is the only microstate in the $k = 0$ macrostate, $w_0 = 1$. The top right is the $k = 1$ macrostate with 6 microstates, $n_0 = 1, n_1 = 1, n_2 = 1, n_3 = 0$. On the bottom is the $k = 2$ macrostate with 3 microstates, $n_0 = 2, n_1 = 0, n_2 = 0, n_3 = 1$.

In general the number of microstates is given by

$$\Omega = \sum_k w_k = \frac{(N + n_{\max} - 1)!}{n_{\max}! \, (N - 1)!}. \tag{4.5}$$

When $N = 3$ and $n_{\max} = 3$ this becomes $\Omega = 10$.

If the oscillators are indistinguishable, but allowed to occupy the same state, then there are less microstates, in the $k = 1$ macrostate we can no longer tell the difference between the 6 microstates. While when the oscillators are not allowed to occupy the same state there is only the $k = 1$ macrostate. The $N = 3, E = 3\varepsilon$ case of indistinguishable oscillators is shown in Figure 11.
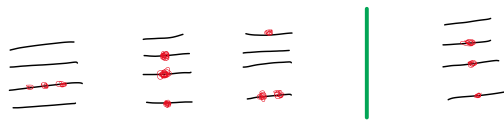
Figure 11: The macro states for 3 indistinguishable harmonic oscillators.

Note that the number of microstates is always smaller when the entities, here oscillators, are *indistinguishable*. There are more accessible states if there is no restriction on occupation number.

4.4 Particle in a cubic box

Consider another familiar situation, that of quantum mechanical particles in a cubic box. Assume 3 particles in a cubic box with side length L, volume $V = L^3$. From the Schrödinger

equation $H\psi = E\psi$ the eigenfunctions and eigenvalues are found to be:

$$\psi_{n_x,n_y,n_z}(x, y, z) = c \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right), \tag{4.6}$$

$$E_{n_x,n_y,n_z} = \frac{\left(n_x^2 + n_y^2 + n_z^2\right)\pi^2 \hbar^2}{2mL^2}, \tag{4.7}$$

the quantum numbers describing the states are n_x, n_y, n_z, these are positive integers $1, 2, 3, \cdots$. The quantum numbers determine what form the wavefunction has in each direction.

Include figure of the cubic box

It is conventional to redefine the energy so that the lowest energy state $n_x, n_y, n_z = 1, 1, 1$ is thought of as the zero energy state and the energies of the other states are given in terms of $E = E_{1,1,1}$. The energy spectrum is given in Figure 12. The g_i's are the degeneracy of energy level ε_i, that is how many states have the same energy. These degenerate states are all counted separately.
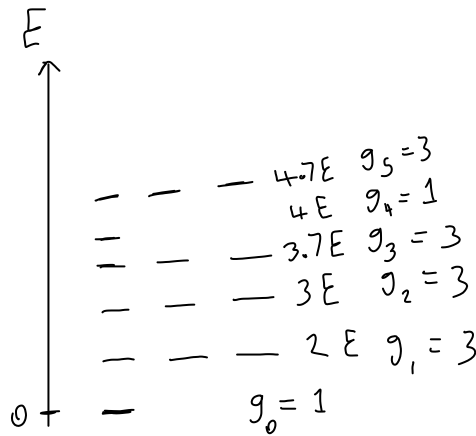
Figure 12: The energy spectrum of a quantum mechanical harmonic oscillator.

The total number of microstates Ω depends on U, V, N and whether particles are distinguishable or indistinguishable. As N and or U increases the number of microstates increases massively, the number of microstates also increases. This can be seen in the oscillator example if you considered $N = 4, E = 4\varepsilon$ or $N = 3, E = 4\varepsilon$.

As a generic example, consider a set of energy levels, ε_i, with degeneracies g_i and occupation numbers n_i. The example of an arbitrary microstate is shown in 13.

The *general fundamental assumption of statistical thermodynamics* can be stated as: In an isolated system all accessible quantum states are assumed to be equally probably. e.g. all microstates are equally probable.

A microstate is accessible if its properties are compatible with the physical specifications of the system; it satisfies the constraints

$$N = \sum_i n_i, \qquad U = \sum_i n_i \varepsilon_i. \tag{4.8}$$

22
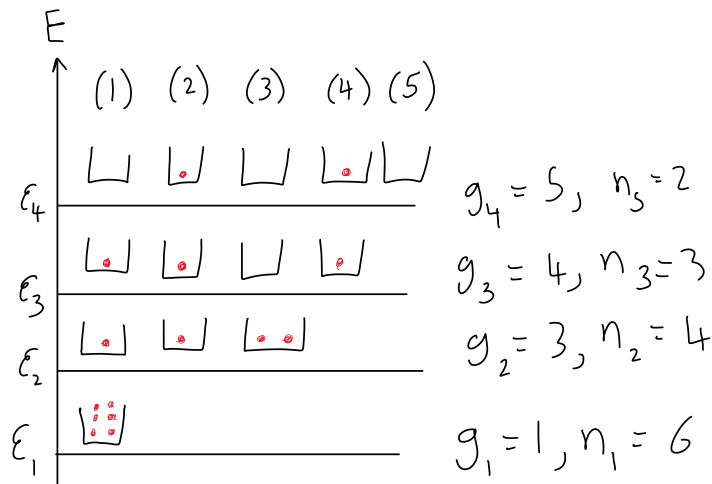
Figure 13: The energy spectrum of a quantum mechanical harmonic oscillator.

In other words the overall energy of a microstate must be in the range of energy specified for the energy of the system. The number of particles must also be in the same range as the specified number of particles of the system[8].

4.5 * Distinguishable Particles

This is essentially a reproduction of parts if Chapter 2 of [Gue07]. However, I think that it is important enough to state here as well. We will come back to some of these results later in the course.

Consider a system of N indistinguishable, localised, particles in a fixed volume V, with fixed internal energy, U. The system is mechanically and thermally isolated so that T, S and other stte ariables are well defined.

The one particle states are labelled by an integer $i = 0, 1, 2, \ldots$, the corresponding energies ε_i may have *degeneracies*, g_i meaning that multiple states have the same energy. States depend on the volume per particle $\frac{V}{N}$. The distribution is the set of occupation numbers, $\{n_i\}$ such that

$$N = \sum_i n_i, \qquad U = \sum_i n_i \varepsilon_i. \tag{4.9}$$

As prticles are distinguishable they can be counted. A microstate then specifies the state for each distinct particle. We want to know the total number of microstates for an allowable microstate, e.g possible arrangements of N objects into piles with n_i objects in the i'th pile; The answer is

$$w_k = \frac{N!}{\prod_i n_i!}. \tag{4.10}$$

---

[8]These can be summarised as $\frac{\delta U}{U} \ll 1$ and $\frac{\delta N}{N} \ll 1$. In practice we will just impose the constraints.

The averaging postulate states that the thermal distribution is obtained by evaluating the average distribution $\{n_i\}_{\mathrm{av}}$. e.g. weighted average of all possible distributions.

The key point is that there is one particular distribution $\{n_i^*\}$ which is much more probable than any others. e.g w_k is sharply peaked around $\{n_i^*\}$. The total number of microstates, $\Omega = \sum_k w_k$ can be approximated by the maximum value of w_k, w_k^* for $\{n_i^*\}$.

This now means hat we need to find w_k^* and $\{n_i^*\}$. It is easier, and more convenient to work with $\log(w_k)$:

$$\log(w_k) = \log(N!) - \sum_i \log(n_i),$$

$$= (N \log N - N) - \sum_i (n_i \log n_i - n_i),$$

where we have assumed that the n's are large enough to use Stirling's approximation[9]. To find the maximum differentiate this, and use that N is constant;

$$d\log(w_k) = 0 - \sum_i \left(dn_i \log n_i + \frac{n_i dn_i}{n_i} - dn_i \right)$$

$$= - \sum_i dn_i \log n_i$$

$$= - \sum_i \log n_i^* dn_i \overset{!}{=} 0$$

In the last line we have replaced n_i with it's maximum value n_i^*, and dn_i being the distance between the value n_i and the maximum value. The $\overset{!}{=} 0$ is because we are solving for the maximum. Differentiating the constraints leads to the conditions:

$$0 = dN = \sum_i dn_i, \tag{4.11}$$

$$0 = dU = \sum_i \varepsilon_i dn_i \tag{4.12}$$

Impose these using Lagrange multipliers, α, β,

$$d\log w_k + \alpha \sum_i dn_i + \beta \sum_i \varepsilon_i dn_i = \sum_i \left(-\log n_i^* + \alpha + \beta \varepsilon_i \right) dn_i = 0, \tag{4.13}$$

$\forall \alpha, \beta$. Can write this such that each term is zero, as the dn_i are independent for each i. This fixes α and β. Implies that n_i^* is given by

$$\left(-\log n_i^* + \alpha + \beta \varepsilon_i \right) = 0, \tag{4.14}$$

for specific, but as yet undetermined α and β,

$$\Rightarrow n_i^* = \exp\left(\alpha + \beta \varepsilon_i \right). \tag{4.15}$$

---

[9]The approximation is that $N! \simeq (2\pi N)^{\frac{1}{2}} N^N \exp(-N)$, or taking logarithms and discounting the constant term, $\log N \simeq N \log N - N$.

This is known as the Boltzmann distribution. Determining α and β is the next challenge. They re determined by the constraints.

$$N = \sum_i n_i = e^\alpha \sum_i e^{\beta \varepsilon_i}, \tag{4.16}$$

with $e^\alpha = A$ a normalisation factor. Can also write $A = \frac{N}{Z}$ for the partition function

$$Z = \sum_i e^{\beta \varepsilon_i} \tag{4.17}$$

and

$$n_i = \frac{N}{Z} e^{\beta \varepsilon_i}. \tag{4.18}$$

We will see a lot more about the partition function later[10]. The other Lagrange multiplier β is more subtle, it is related to the temperature:

$$U = \sum_i \varepsilon_i n_i = \frac{N}{Z} \sum_i \varepsilon_i e^{\beta \varepsilon_i} \tag{4.19}$$

or

$$\frac{U}{N} = \frac{\sum_i \varepsilon_i e^{\beta \varepsilon_i}}{\sum_i e^{\beta \varepsilon_i}} \tag{4.20}$$

determines β. $\frac{U}{N}$ is the internal energy per particle, and for a given U, V, N macrostate it fully specifies β. Through this we can interpret β. as a potential for the energy.

We will see later that $\beta = \frac{1}{k_B T}$, for k_B Boltzmann's constant. Note that some times there is a minus sign in the definition of β, for example in [Gue07].

4.6 Fermions and Bosons

The nature of the entities that make up a many body system has a profound effect on the states of the system. Quantum theory results in two rules for non-interacting particles:

(1) A state can be occupied by an integral number of particles of the same species, including zero. These particles are called Bosons, e.g. photons of light.

(2) A state can be occupied by 0 or 1 particles of the same species. These particles are called Fermions, e.g. electrons and protons.

The second rule is known as the Pauli exclusion principle, it says that no two fermionic particles can have identical quantum numbers.

There is a classical limit where the quantum nature of the particles does not matter for the thermal average occupancy. All that matters is if they can occupy the same state or not. We will return to the quantum nature later on in the course.

---

[10]This is in fact the partition function for the canonical ensemble, or the canonical partition function. We will discuss the different ensembles later.

The thermodynamic probability, w_k, of a macrostate depends on the particle statistics (Bose-Einstein or Fermi-Dirac) obeyed by the system. The probability of finding a system in a specific macrostate k is

$$p_k = \frac{w_k}{\Omega}. \tag{4.21}$$

The probability of finding a system in a specific microstate i is $p_i = \frac{1}{\Omega}$.

4.6.1 Bose-Einstein Statistics

We want to describe the distribution of a bosonic system. Particles are indistinguishable, non-interacting and there is no restriction on the number of particles that can occupy any state. While the particles are indistinguishable, the states are known and distinguishable. We want to derive the thermodynamic probabilities, w_k, and the number of microstates, Ω_{BE}.

Figure 14: A generic configuration of bosons with energy ε_i. Pretending the particles are distinguishable, this configuration corresponds to the sequence $1ab2c34def$.

A generic energy level of a bosonic system is shown in Figure 14, the states are labelled by the numbers and pretending that we can distinguish the particles we label them $a, b, c, \ldots$. Every energy level thus corresponds to a sequence of letters and numbers:

$$1ab2c34def \tag{4.22}$$

- The degeneracy g_i is the number of numbers in the sequence.

- The occupation number n_i is the number of letters in the sequence.

Such a sequence always starts with a number, so there are $g_i - 1 + n_i$ symbols left to specify. Generically for N objects there are $N!$ ways to arrange them, e.g. $3! = 6$ ways to arrange three objects. Thus after specify the initial number there are $(g_i - 1 + n_i)!$ ways to arrange the rest of the sequence. There are g_i possible starting numbers so the number of sequences is $g_i (g_i - 1 + n_i)!$.

We seem to be done, but this actually over counts the number of sequences. For example

$$[1ab]\,[2c]\,[3]\,[4def] = [3]\,[1ab]\,[4def]\,[2c], \tag{4.23}$$

as what matters is which states are occupied and what the occupation numbers are rather than how the states are ordered. There are g_i such groups so $g_i!$ ways to order the groups. Thus we need to divide by $g_i!$ to avoid counting identical states multiple times.

Finally we need to remember that the particles are indistinguishable, this requires dividing by the number of ways of ordering n_i particles, $n_i!$.

This implies that the number of possible arrangements for the energy level ε_i is

$$\omega_i = \frac{g_i (g_i - 1 + n_i)!}{g_i! n_i!} = \frac{(g_i - 1 + n_i)!}{(g_i - 1)! n_i!}. \tag{4.24}$$

In Figure 15 the possible configurations for an energy level with $n_i = 2, g_i = 3$ is shown. For
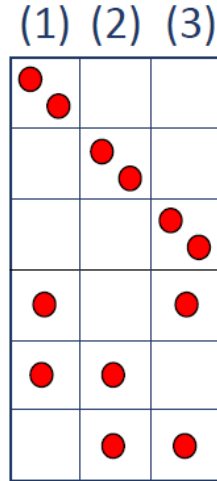
Figure 15: Possible configurations for $n_i = 2$ bosons with $g_i = 3$. Here $\omega_i = \frac{(3-1+2)!}{(3-1)2!} = \frac{4!}{2!2!} = 6$.

each possible configuration of a single energy level, the other energy levels may have any other configuration. Therefore the thermodynamic probability is the product of all the ω_i's:

$$w_{\text{BE}} = w_k = \prod_i \omega_i = \prod_i \frac{(g_i - 1 + n_i)!}{(g_i - 1)! n_i!}, \tag{4.25}$$

and the total number of microstates is $\Omega_{\text{BE}} = \sum_k w_k$.

Example 4.2. Example with $N = 6, U = 6\varepsilon, g_i = 3, \Omega = 1532$

4.6.2   Fermi-Dirac Statistics

In a similar vein to the last section on Bose-Einstein statistics the particles are indistinguishable and non-interacting. However, in contrast to the Boson case the Pauli exclusion principle holds and there is either one or zero particles in each permitted state. The states are again known and distinguishable. We derive the thermodynamic probabilities and the statistical weight.

Consider a generic energy level of a fermionic system, as shown in Figure 17. Pretending that the particles are distinguishable we can assign a sequence of letters and numbers, $1a2b34c5$, which describes the occupation of state i with fermions. Noting the constraint $n_i < g_i$, there are g_i

Figure 16: Possible configurations, and the corresponding thermodynamic probability for $N = 6, U = 6\varepsilon, g_j = 3$. The statistical weight is $\Omega_{BE} = 1532$. $\bar{n}_j = \Omega^{-1} \sum_k (n_j)_k w_k$, is the average occupation number for energy level j.
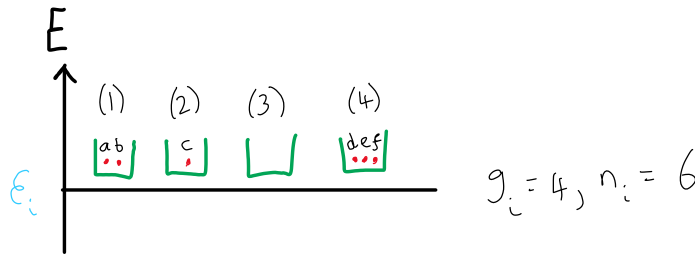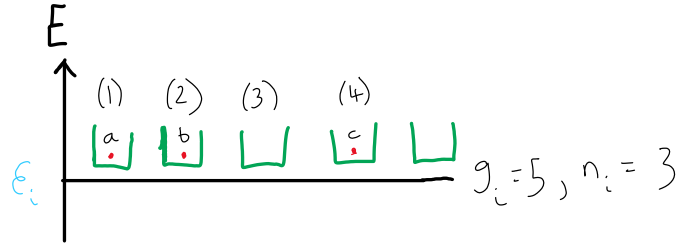

Figure 17: A generic configuration of bosons with energy ε_i. Pretending the particles are distinguishable, this configuration corresponds to the sequence $1ab2c34def$.

options for the first letter/ particle, $g_i - 1$ choices for the second letter/ particle, $\dots g_i - (n_i - 1)$ options to place the last letter/ particle. This implies that there are

$$g_i (g_i - 1) \dots (g_i - (n_i - 1)) \tag{4.26}$$

ways to place n_j distinguishable fermions into the g_i states. Next observe that

$$g_i! = g_i (g_i - 1) \dots (g_i - (n_i - 1)) (g_i - n_i) \cdots 2 \times 1 = g_i (g_i - 1) \dots (g_i - (n_i - 1)) (g_i - n_i)!. \tag{4.27}$$

The first n_i terms gives the number of sequences that we found above, thus the rewriting

$$g_i (g_i - 1) \dots (g_i - (n_i - 1)) = \frac{g_i!}{(g_i - n_i)!} \tag{4.28}$$

gives a more convenient expression for the number of sequences. Recalling the particles are really indistinguishable we divide by $n_i!$ to avoid over counting and find

$$\omega_i = \frac{g_i!}{(g_i - n_i)!n_i!}. \tag{4.29}$$
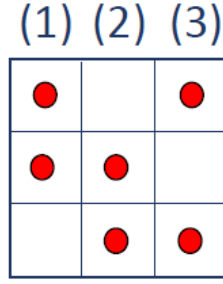
Figure 18: Possible configurations for $n_i = 2, g_i = 3$ fermions. $\omega_i = \frac{3!}{(3-2)!2!} = \frac{6}{2} = 3$.

Figure 15 shows the possible configurations for an energy level with $n_i = 2$ fermions and $g_i = 3$.

Finally taking the product of this for all energy levels gives the thermodynamic probability,

$$w_k = \prod_i \omega_i = \prod_i \frac{g_i!}{(g_i - n_i)!n_i!}. \tag{4.30}$$

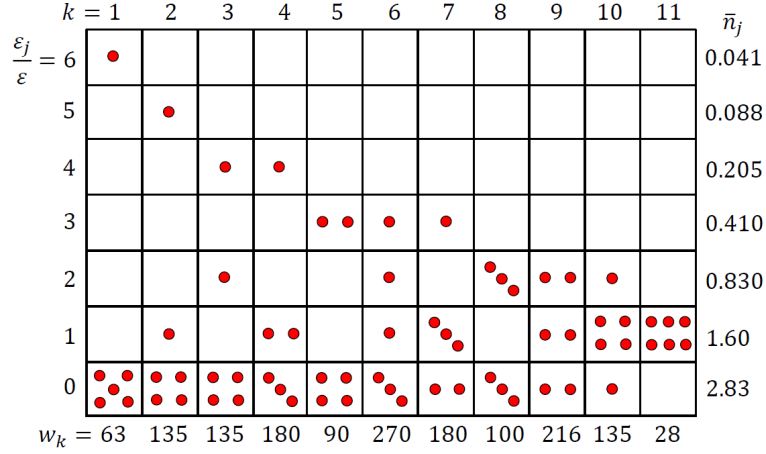**Example 4.3. Example with** $N = 6, U = 6\varepsilon, g_i = 3, \Omega_{FD} = 73$
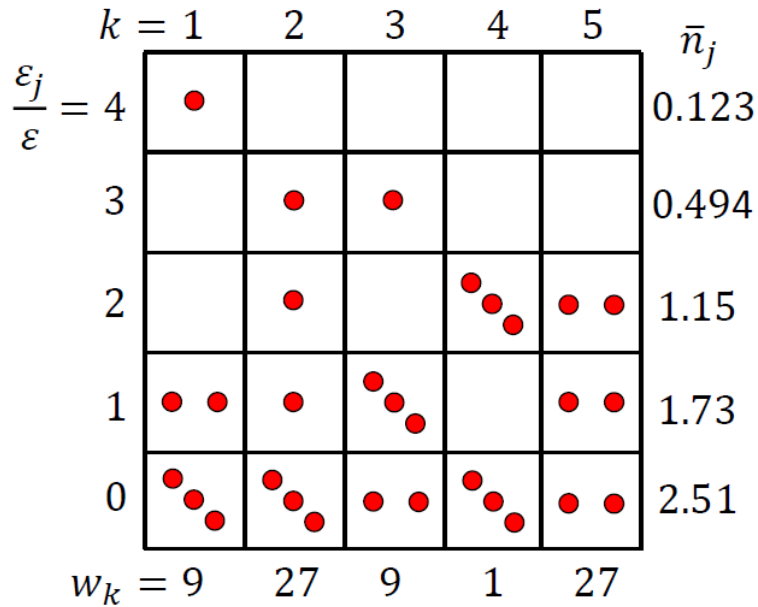
Figure 19: Possible configurations, and the corresponding thermodynamic probability for $N = 6, U = 6\varepsilon, g_j = 3$. The statistical weight is $\Omega_{FD} = 73$. $\bar{n}_j = \Omega^{-1} \sum_k (n_j)_k w_k$, is the average occupation number for energy level j.

## 4.7 Maxwell-Boltzmann Statistics

Now we turn to classical particles. Here the particles are *distinguishable*, non-interacting, and there is no restriction on how many particles can occupy a state. Again the states are

distinguishable. Before finding w_k we first give the example in Figure 20 of $n_i = 2, g_i = 3$:

(1)	(2)	(3)
a b		
	a b	
		a b
a	b	
b	a	
a		b
b		a
	a	b
	b	a

Figure 20: Possible configurations for $n_i = 2, g_i = 3$ classical particles. $\omega_i = 9 = 3^2$

For all levels we thus have $\prod_i \omega_i = \prod_i g_i^{n_i}$. We also need to take account of how the particles are distributed between the energy levels. For N classical particles divided in to piles with n_i in the i'th pile, the number of arrangements is

$$\frac{N!}{n_1! n_2! \dots} = \frac{N!}{\prod_i n_i!}. \tag{4.31}$$

Combining all of this together gives

$$w_k = N! \prod_i \frac{g_i^{n_i}}{n_i!}. \tag{4.32}$$

Example 4.4. Example with $N = 6, U = 6\varepsilon, g_i = 3, \Omega_{MB} = 3.37 \times 10^5$

5 Thermodynamic Ensembles

Figures to be included.

There are three types of thermodynamic systems, and each corresponds to what is called an *ensemble*. The difference comes from which macrostcopic quantities are conserved.

1. Isolated: no exchange of energy or mass with the surroundings. e.g. a closed thermos flask. Called the microcanonical ensemble: U, V, N all fixed for the total system.

2. Closed: Exchange of energy with the surroundings is possible, but no exchange of mass. e.g. closed fridge or heating system. Called the canonical ensemble: V, N fixed, bit U fluctuates.

3. Open: Exchange of energy and mass with the surroundings is possible. e.g. a cell membrane. Called the grand canonical ensemble V fixed, but N and U fluctuates.

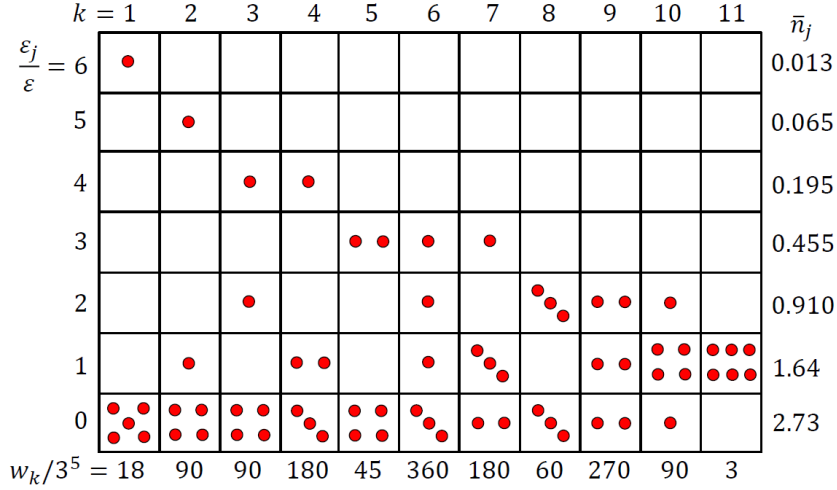|	k = 1	2	3	4	5	6	7	8	9	10	11	$\bar{n}_j$
$\frac{\varepsilon_j}{\varepsilon} = 6$	●											0.013
5		●										0.065
4			●	●								0.195
3					●●	●	●					0.455
2			●				●	●●	●●	●		0.910
1		●		●●	●		●	●●		●●	●●●	1.64
0	●●●●●	●●●●	●●●●	●●●	●●●●	●●●	●●	●●	●●	●		2.73
$w_k/3^5 =$	18	90	90	180	45	360	180	60	270	90	3	

Figure 21: Possible configurations, and the corresponding thermodynamic probability for $N = 6, U = 6\varepsilon, g_j = 3$ classical particles. The statistical weight is $\Omega_{FD} = 3.37 \times 10^5$. $\bar{n}_j = \Omega^{-1} \sum_k (n_j)_k w_k$, is the average occupation number for energy level j.

5.1 Thermal equilibrium and entropy revisited

Consider a closed system consisting of two subsystems in thermal contact with constant total energy, $U = U_1 + U_2$, no exchange of particles. The statistical weight $\Omega(N, U)$ of the combined system is given by

$$\Omega(N, V) = \sum_{U_1} \Omega_1 (N_1, U_1) \Omega_2 (N_2, U - U_1). \tag{5.1}$$

The first factor, $\Omega_1 (N_1, U_1)$ is the number of microstates in system 1 at energy U_1. For a given U the number of accessible microstates in a macrostate is the product $\Omega_1 (N_1, U_1) \Omega_2 (N_2, U - U_1)$. The sum over all possible values of system 1's energy, $U_1 \leq U$ results in $\Omega(N, V)$.

The largest term in the sum governs the properties of the entire system in thermal equilibrium. To find this maximum value we need to find the stationary values of Ω subject to infinitesimal change in the subsystem energies, e.g. $d\Omega = 0$.

As N is fixed the differential of Ω is

$$d\Omega = \left(\frac{\partial \Omega}{\partial U_1} \right)_{N_1, U_2} dU_1 + \left(\frac{\partial \Omega}{\partial U_2} \right)_{N_1, U_1} dU_2 \overset{!}{=} 0. \tag{5.2}$$

In equilibrium the total energy is constant, $0 = dU = dU_1 + dU_2$ which implies that $dU_1 = -dU_2$ and

$$d\Omega = \left(\left(\frac{\partial \Omega}{\partial U_1} \right)_{N_1, U_2} - \left(\frac{\partial \Omega}{\partial U_2} \right)_{N_1, U_1} \right) dU_1. \tag{5.3}$$

Recalling that $\Omega = \Omega_1(U_1)\Omega_2(U_2)$ the equilibrium condition becomes

$$\Omega_2 \left(\frac{\partial \Omega_1}{\partial U_1} \right)_{N_1, U_2} = \Omega_1 \left(\frac{\partial \Omega_2}{\partial U_2} \right)_{N_1, U_1}, \tag{5.4}$$

divide both sides by Ω to find

$$\frac{1}{\Omega_1}\left(\frac{\partial\Omega_1}{\partial U_1}\right)_{N_1,U_2} = \frac{1}{\Omega_2}\left(\frac{\partial\Omega_2}{\partial U_2}\right)_{N_1,U_1}. \tag{5.5}$$

This can be rewritten as

$$\left(\frac{\partial\log\Omega_1}{\partial U_1}\right)_{N_1,U_2} = \left(\frac{\partial\log\Omega_2}{\partial U_2}\right)_{N_1,U_1} \tag{5.6}$$

which motivates introducing the quantity,

$$\sigma(N,U) = \log\Omega, \tag{5.7}$$

known as the fundamental entropy.

The previous thermodynamic equilibrium condition was that $\frac{1}{T_1} = \frac{1}{T_2}$, which suggests that $\frac{1}{T_i} = k_B\left(\frac{\partial\sigma_i}{\partial U_1}\right)_{N_1,U_2}$. The constant of proportionality k_B is Boltzmann's constant $k_B = 1.38 \times 10^{-23}$. Often, for example in [KK80], $\frac{1}{\tau} = \left(\frac{\partial\sigma_i}{\partial U_1}\right)_{N_1,U_2}$ is called the fundamental temperature and is related to the measure, or thermodynamic temperature through $\tau = k_B T$. Identifying $S = k_B\sigma$ as the entropy we recover the familiar relation $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)$. This implies the relationship

$$S = k_B\log\Omega, \tag{5.8}$$

in words this says that entropy is the logarithm of the number of microstates accessible to the system.

An immediate consequence of this is that any increase in the statistical weight Ω will increase the entropy. Some possibilities for how to do this are given in Figure 22.
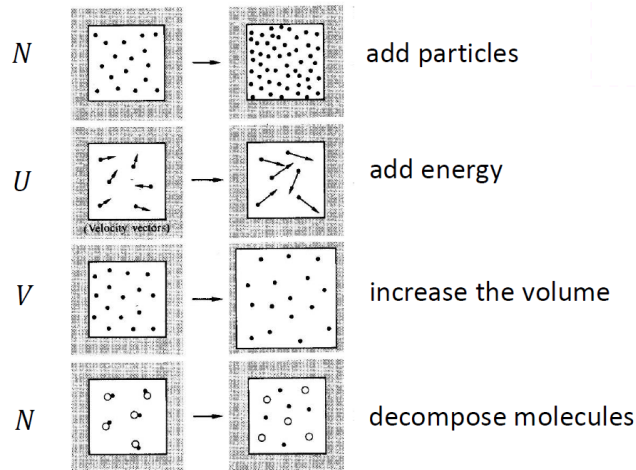

Figure 22: Some of the ways that Ω, and hence the entropy, can be increased.

The equilibrium term dominates the sum in Equation (5.1).

5.2 Boltzmann Factor and the Partition Function

A central object in statistical physics is the *partition function*, which measures the average number of accessible states at a given temperature for a system in equilibrium. To understand the partition function we start by considering a closed total system with energy U_0, consisting of two parts; a reservoir $\mathcal{R}$, and a system $\mathcal{S}$. The system could consist of just one particle, or of N-particles.

The probability of the system being in a particular state, i, is

$$p(\varepsilon_i) = \frac{\Omega_{\mathcal{R}}(U_0 - \varepsilon_i)}{\Omega_{\mathcal{R}+\mathcal{S}}(U_0)}. \tag{5.9}$$

The ratio of two probabilities, e.g. comparing the probability of the system being in state 1 to the probability of the system being in state 2, is

$$\frac{p(\varepsilon_1)}{p(\varepsilon_2)} = \frac{\Omega_{\mathcal{R}}(U_0 - \varepsilon_1)}{\Omega_{\mathcal{R}}(U_0 - \varepsilon_2)} = \frac{e^{\sigma_{\mathcal{R}}(U_0 - \varepsilon_1)}}{e^{\sigma_{\mathcal{R}}(U_0 - \varepsilon_2)}} = e^{\Delta\sigma_{\mathcal{R}}}. \tag{5.10}$$

Here $\Delta\sigma_{\mathcal{R}}$ is the difference in the fundamental entropy of the reservoir between the system being in state 1 or state 2. For a suitably large reservoir we can assume that $U_0 \gg \varepsilon_i$, thus $\sigma_{\mathcal{R}}$ can be Taylor expanded:

$$\sigma_{\mathcal{R}}(U_0 - \varepsilon_i) = \sigma_{\mathcal{R}}(U_0) - \varepsilon_i \left(\frac{\partial\sigma_{\mathcal{R}}}{\partial U_0}\right)_{V,N} + \cdots = \sigma_{\mathcal{R}}(U_0) - \frac{\varepsilon}{\tau}, \tag{5.11}$$

$$\Rightarrow \Delta\sigma_{\mathcal{R}} = -\frac{(\varepsilon_1 - \varepsilon_2)}{\tau} = -\beta(\varepsilon_1 - \varepsilon_2). \tag{5.12}$$

In the above we have made use of the relationship $\left(\frac{\partial\sigma_{\mathcal{R}}}{\partial U_0}\right)_{V,N} = \frac{1}{\tau}$. The ratio of probabilities can now be expressed as

$$\frac{p(\varepsilon_1)}{p(\varepsilon_2)} = \frac{e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_2}}, \tag{5.13}$$

from which we read off that

$$p(\varepsilon_1) \propto e^{-\beta\varepsilon_1} = e^{-\frac{\varepsilon_1}{k_B T}}, \tag{5.14}$$

with the exponential factor known as the Boltzmann factor. The Boltzmann factor is the thermodynamic probability of the system being in a state with energy ε_i, to obtain a true probability we need to normalise by dividing by the sum over all of these Boltzmann factors. This sum is known as the partition function Z:

$$Z = \sum_i e^{-\beta\varepsilon_i} = \sum_j g_j e^{-\beta\varepsilon_j}, \tag{5.15}$$

where the first sum is over all states i in the system, while the second sum takes account of the degeneracy of the energy levels and is a sum over the energy levels j.

The probability of finding the system at energy ε_j is then

$$p(\varepsilon_j) = \frac{g_j e^{-\beta\varepsilon_j}}{Z} = \frac{n_j}{N}, \tag{5.16}$$

with n_j the occupation number of energy level j and N the total particle number. Observe that $\sum_j p(\varepsilon_j) = \frac{Z}{Z} = 1$, so it is indeed a probability.

Another useful concept is the thermal average, or ensemble average, of a thermodynamic quantity. This average is denoted

$$\langle X \rangle = \sum_j X_j p(X_j), \tag{5.17}$$

for a quantity X. It is most common to encounter the thermal average energy[11]

$$U = \langle \varepsilon \rangle = \sum_j \varepsilon_j p(\varepsilon_j), \tag{5.18}$$

note that here U is the system energy and **not** the energy of the systems plus the reservoir.

A major boon of working with the partition function is that many thermodynamic quantities can be constructed from it by taking derivatives. Consider the thermal average energy U:

$$
\begin{aligned}
U &= \langle \varepsilon \rangle \\
&= \frac{1}{Z} \sum_j \varepsilon_j g_j e^{-\beta \varepsilon_j}, \quad \text{using the definition of } p(\varepsilon_j) \\
&= -\frac{1}{Z} \frac{dZ}{d\beta}, \quad \text{using } \frac{dZ}{d\beta} = -\sum_j g_j \varepsilon_j e^{-\beta \varepsilon_j} \\
&= -\frac{d \ln Z}{d\beta},
\end{aligned}
$$

giving that

$$U = -\frac{d \ln Z}{d\beta}. \tag{5.19}$$

On the second problem sheet you showed that

$$F = -\beta^{-1} \ln Z. \tag{5.20}$$

These are just two examples of thermodynamic quantities that can de derived as thermal averages from the partition function. You will meet others on the problem sheets and in other courses.

Example 5.1. Ideal monatomic gas
Let us now consider how to actually compute the partition function for a system. Consider the case of 1 atom of mass m allowed to move freely in a cubic box of volume $V = XYZ$. In this case the partition function is known as the translational partition function as we are considering translational motion of the atom within the box. This enables us to identify the energy of the atom with the energy levels of a particle in a box. If allowed the atom to vibrate or rotate then this will change the energy[12]. The partition function is thus

$$Z_1 = \sum_n e^{-\beta \varepsilon_n}, \quad \varepsilon_n = \varepsilon_{n_x} + \varepsilon_{n_y} + \varepsilon_{n_z}, \tag{5.21}$$

---

[11]When we consider open systems in the next section we will also encounter the thermal average of the particle number.

[12]In a first approximation, allowing vibration will result in a harmonic oscillator like contribution to the energy. However, this complicates the problem so we will disregard it for now.

with n_x, n_y, n_z the quantum numbers describing the state of the system, the energy is the sum of the translational energy in each direction. Expanding this we have that

$$Z_1 = \sum_n e^{-\beta\left(\varepsilon_{n_x} + \varepsilon_{n_y} + \varepsilon_{n_z}\right)} = Z_{1x} Z_{1y} Z_{1z}, \tag{5.22}$$

where

$$Z_{1x} = \sum_n e^{-\beta \varepsilon_{n_x}} \tag{5.23}$$

is the one dimensional translation partition function for the x-direction, and Z_{1y}, Z_{1z} are the same for the y and z directions. Observe that while energies are additive, partition functions are multiplicative! For a one-dimensional box of length X the quantum mechanical energy levels are

$$\varepsilon_{n_x} = \frac{n_x^2 h^2}{8mX^2}, \tag{5.24}$$

which means that Equation (5.23) becomes

$$Z_{1x} = \sum_{n=0}^{\infty} e^{-\beta \frac{n_x^2 h^2}{8mX^2}}, \tag{5.25}$$

by convention the zero point energy, ε_0 is set to zero so contributes 1 to the sum. Provided the spacing between the energy levels is small in comparison to $k_B T$ we can take a continuum limit and replace the sum with an integral,

$$Z_{1x} = \int_0^\infty \exp\left(-\beta \frac{n_x^2 h^2}{8mX^2}\right) dn_x. \tag{5.26}$$

This integral can be solved using the substitution

$$a^2 = \beta \frac{n_x^2 h^2}{8mX^2}, \quad \Rightarrow dn_x = \sqrt{\frac{8mX^2}{\beta h^2}} da, \tag{5.27}$$

which turns the integral into a Gaussian integral and gives

$$Z_{1x} = \sqrt{\frac{8mX^2}{\beta h^2}} \int_0^\infty \exp\left(-a^2\right) da = \sqrt{\frac{8mX^2}{\beta h^2}} \frac{\sqrt{\pi}}{2} = \sqrt{\frac{2m\pi}{\beta h^2}} X \tag{5.28}$$

as the one dimensional translational partition function. An analogous calculation gives the y and z terms.

Putting everything together we have that

$$Z_1 = Z_{1x} Z_{1y} Z_{1z} = \left(\frac{2m\pi}{\beta h^2}\right)^{\frac{3}{2}} XYZ = n_Q n, \tag{5.29}$$

where

$$n = \frac{1}{V} = \frac{1}{XYZ}, \tag{5.30}$$

35

is the number density of 1 atom per volume, and

$$n_Q = \left(\frac{2m\pi}{\beta h^2}\right)^{\frac{3}{2}} \tag{5.31}$$

is the quantum concentration. This is the concentration associated with 1 atom in a cube with side length equal to the thermal average of the de Broglie wavelength, $l = \langle\lambda\rangle = \frac{h}{m\langle v\rangle}$.

The size of $\frac{n}{n_Q}$ is a criteria for whether a gas is in a quantum or classical regime. When $\frac{n}{n_Q} \ll 1$ the gas is in the classical regime governed by Boltzmann statistics. An *Ideal gas* is defined as a gas of non-interacting particles in the classical regime.

An example of an ideal gas is Helium at room temperature, $296K$, and pressure 1atm $=$ 101325Pa. Here we have that[13]

$$n = 2.48 \times 10^{19}\text{cm}^{-3}, \tag{5.32}$$
$$n_Q = 7.71 \times 10^{24}\text{cm}^{-3}. \tag{5.33}$$

The ratio is $\frac{n}{n_Q} \simeq 3.2 \times 10^{-6} \ll 1$ so we are in the classical regime and He is an ideal gas. This means that the number of Helium aoms is much smaller than the number of available quantum states.

Example 5.2. N-particle partition function
For a gas of N atoms we proceed as in the one-particle case, but now we are splitting the partition function into the product of the one-particle partition functions for each particle[14]. This happens because the N-particle energy of state i splits into the sum of the energies of each particle in the state
$$\varepsilon_i = \varepsilon_i^{(1)} + \varepsilon_i^{(2)} + \varepsilon_i^{(3)} + \cdots + \varepsilon_i^{(N)}, \tag{5.34}$$

here we are pretending that the particles are distinguishable so that we can label them $1, 2, 3, \ldots, N$. If the particles are indistinguishable we need to divide the product of one-particle partition functions by $\frac{1}{N!}$ to avoid over counting by treating the different orders as distinct configurations. The N-particle partition function is thus

$$Z_N = \left(\sum_i e^{-\beta\varepsilon_i^{(1)}}\right)\left(\sum_i e^{-\beta\varepsilon_i^{(2)}}\right)\cdots\left(\sum_i e^{-\beta\varepsilon_i^{(N)}}\right) = Z_1^{(1)}Z_1^{(2)}\ldots Z_1^{(N)}. \tag{5.35}$$

We thus have that

$$Z_N = \begin{cases} (Z_1)^N & \text{for distingushable particles,} \\ \dfrac{1}{N!}(Z_1)^N & \text{for indistingushable particles.} \end{cases} \tag{5.36}$$

---

[13]When giving $n = \frac{1}{V}$ we are cheating slightly, really we should specify the volume and find N from this. Instead we are assuming that we have an ideal gas and using the equation $p = nk_BT$ to compute the number density for the given pressure and temperature.

[14]To do this we require the particles to be non-interacting, or at least so weakly interacting that we can forget about the interaction.

5.3 Gibbs Factor and Grand Partition Function

When we discussed the Boltzmann factor we were considering a closed system able to exchange heat with a large reservoir. What happens for an open system?

Consider again a total system, with energy U_0 and N_0 particles, consisting of a reservoir $\mathcal{R}$ and a system $\mathcal{S}$. The probability for the particle to be in state i with N particles and energy $\varepsilon_{i(N)}$ is

$$p(N, \varepsilon_{i(N)}) \propto \Omega_\mathcal{R}\left(N_0 - N, U_0 - \varepsilon_{i(N)}\right). \tag{5.37}$$

The notation $\varepsilon_{i(N)}$ is used to make it clear that we are talking about the energy of state i of the N particle system. If the particles are non-interacting, then the energy of an N-particle state is N times the energy of a 1 particle state and we can use the simpler notation ε_i. We will tend to use the second notation but it is occasionally convenient to use the first as it clears up that we are talking about the probability to find the system in a given microstate. Writting it out in full the probability is proportional to the number of microstates of the total system, $\mathcal{R} + \mathcal{S}$ consistent with $\mathcal{S}$ being in state $i(N)$. However, as we are specifying the state of $\mathcal{S}$, we find that this is $\Omega_{\mathcal{R}+\mathcal{S}} = \Omega_\mathcal{R}(N_0 - N, U_0 - \varepsilon_{i(N)}) \times 1$. In other words the total number of states accessible to the reservoir is the same as the number of states accessible to $\mathcal{R} + \mathcal{S}$ as we have specified the state of $\mathcal{S}$.

This implies that the ratio of probabilities is

$$\frac{p(N_1, \varepsilon_{1(N_1)})}{p(N_2, \varepsilon_{2(N_2)})} = \frac{\Omega_\mathcal{R}\left(N_0 - N_1, U_0 - \varepsilon_{i(N_1)}\right)}{\Omega_\mathcal{R}\left(N_0 - N_1, U_0 - \varepsilon_{2(N_2)}\right)} = e^{\Delta\sigma_\mathcal{R}}, \tag{5.38}$$

with $\Delta\sigma_\mathcal{R}$ the difference between the fundamental entropies of the two states. The approach is again to assume that the reservoir is sufficiently large compared to the system that $U_0 \gg \varepsilon_{1(N_1)}, \varepsilon_{2(N_2)}$ and $N_0 \gg N_1, N_2$. This enables us to Taylor expand the fundamental entropy,

$$\sigma_\mathcal{R}\left(N_0 - N, U_0 - \varepsilon_{i(N)}\right) \simeq \sigma_\mathcal{R}\left(N_0, U_0\right) - N\left(\frac{\partial\sigma_\mathcal{R}}{\partial N_0}\right)_{U_0} - \varepsilon\left(\frac{\partial\sigma_\mathcal{R}}{\partial U_0}\right)_{N_0}. \tag{5.39}$$

Next recall that[15]

$$\left(\frac{\partial\sigma_\mathcal{R}}{\partial N_0}\right)_{U_0} = \frac{1}{k_B}\left(\frac{\partial S_\mathcal{R}}{\partial N_0}\right)_{U_0} = -\frac{\mu}{k_B T} = -\frac{\mu}{\tau}, \tag{5.40}$$

$$\left(\frac{\partial\sigma_\mathcal{R}}{\partial U_0}\right)_{N_0} = \frac{1}{k_B}\left(\frac{\partial S_\mathcal{R}}{\partial U_0}\right)_{N_0} = \frac{1}{k_B T} = \frac{1}{\tau}, \tag{5.41}$$

so we can write

$$\sigma_\mathcal{R}\left(N_0 - N, U_0 - \varepsilon_{i(N)}\right) \simeq \sigma_\mathcal{R}\left(N_0, U_0\right) + \frac{\mu N}{\tau} - \frac{\varepsilon}{\tau}. \tag{5.42}$$

Doing this for $\Delta\sigma_\mathcal{R}$ we find

$$\Delta\sigma_\mathcal{R} = \frac{\mu\left(N_1 - N_2\right)}{\tau} - \frac{\left(\varepsilon_1 - \varepsilon_2\right)}{\tau}, \tag{5.43}$$

---

[15]These relationships are true for the reservoir. However, as $\mathcal{R}$ and $\mathcal{S}$ are in equilibrium they are at the same temperature and have the same chemical potential.

and the ratio of probabilities is thus

$$\frac{p(N_1, \varepsilon_1)}{p(N_2, \varepsilon_2)} = \frac{\exp\left((N_1\mu - \varepsilon_1)\beta\right)}{\exp\left((N_2\mu - \varepsilon_2)\beta\right)}. \tag{5.44}$$

The exponential factor $\exp\left((N\mu - \varepsilon_{i(N)})\beta\right)$ is known as the Gibbs factor. It is proportional to the probability that the system $\mathcal{S}$ is in state i with N particles and energy $\varepsilon_{i(N)}$.

Summing over the possible Gibbs factors gives rise to a partition function, called the *Grand partition function*. This is the normalising factor which turns the Gibbs factors into probabilities, just like the canonical partition function did for the Boltzmann factors of a closed system.

The grand partition function is

$$\mathcal{Z}(\mu, T) = \sum_{N=0}^{\infty} \sum_{i(N)} \exp\left(\frac{N\mu - \varepsilon_{i(N)}}{k_B T}\right). \tag{5.45}$$

Sometimes the double sum, $\sum_{N=0}^{\infty} \sum_{i(N)}$ is written as $\sum_{ANS}$, where ANS stands for all particles all states. This just signifies that we first sum over the possible particle numbers for the system, and then sum over the possible microstates of the system with the given number of particles.

The absolute probability that the system will be found in microstate i with N particles and energy $\varepsilon_{i(N)}$ is

$$p(N, \varepsilon_{i(N)}) = \frac{\exp\left(\beta\left(N\mu - \varepsilon_{i(N)}\right)\right)}{\mathcal{Z}}. \tag{5.46}$$

This is a true probability since

$$\sum_{N=0}^{\infty} \sum_{i(N)} p(N, \varepsilon_{i(N)}) = \frac{\mathcal{Z}}{\mathcal{Z}} = 1. \tag{5.47}$$

As in the case of the canonical ensemble for open systems there is a thermal (or ensemble) average. If $X(N, i)$ is the value of a variable X when the system has N particles in microstate i then its thermal average, over all N and all microstates, is

$$\sum_{N} \sum_{i(N)} X(N, i) p(N, \varepsilon_{i(N)}) = \sum_{N} \sum_{i(N)} \frac{X(N, i) \exp\left(\beta\left(N\mu - \varepsilon_{i(N)}\right)\right)}{\mathcal{Z}}. \tag{5.48}$$

For a system in diffusive and thermal equilibrium with the reservoir the particle number fluctuates, with the average particle number being

$$\langle N \rangle = \sum_{N} \sum_{i(N)} \frac{N \exp\left(\beta\left(N\mu - \varepsilon_{i(N)}\right)\right)}{\mathcal{Z}}. \tag{5.49}$$

Taking the β derivative of the grand partition function gives

$$\frac{\partial \mathcal{Z}}{\partial \mu} = \beta \sum_{N} \sum_{i(N)} N \exp\left(\beta\left(N\mu - \varepsilon_{i(N)}\right)\right), \tag{5.50}$$

which combines with Equation (5.49) to give

$$\langle N \rangle = \frac{1}{\beta \mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}. \tag{5.51}$$

This is another example of the fact that knowing the partition function for an ensemble enables us to calculate thermodynamic quantities.

A useful related quantity is the fugacity (or activity)

$$\lambda = \exp(\beta \mu). \tag{5.52}$$

Using the fugacity the partition function and the average particle number can be rewritten as

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{i(N)} \lambda^N \exp(-\beta \varepsilon_i), \tag{5.53}$$

$$\langle N \rangle = \lambda \frac{\partial \ln \mathcal{Z}}{\partial \lambda}. \tag{5.54}$$

The thermal average of the energy is another useful quantity to compute in terms of $\ln \mathcal{Z}$, though it is not given as simply as for the canonical ensemble above. We have that

$$U = \langle \varepsilon \rangle = \sum_N \sum_{i(N)} \frac{\varepsilon_i \exp\left(\beta\left(N\mu - \varepsilon_{i(N)}\right)\right)}{\mathcal{Z}}, \tag{5.55}$$

to simplify this note that

$$\langle N \rangle \mu - U = \langle N\mu - \varepsilon \rangle \tag{5.56}$$

$$= \sum_N \sum_{i(N)} (N\mu - \varepsilon_i) \frac{\exp\left(\beta\left(N\mu - \varepsilon_{i(N)}\right)\right)}{\mathcal{Z}} \tag{5.57}$$

$$= \frac{1}{\mathcal{Z}} \frac{\partial \ln \mathcal{Z}}{\partial \beta}, \quad \text{To see this just compute } \frac{\partial \ln \mathcal{Z}}{\partial \beta}. \tag{5.58}$$

Upon substituting in Equation (5.49) this results in

$$U = \frac{\mu}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} - \frac{\partial \ln \mathcal{Z}}{\partial \beta} = \left[\frac{\mu}{\beta} \frac{\partial}{\partial \mu} - \frac{\partial}{\partial \beta}\right] \ln \mathcal{Z}. \tag{5.59}$$

6   Quantum Gases: Fermi-Dirac and Bose-Fermi distributions

In the grand canonical ensemble we can consider a system which consists solely of one state (single particle in the case of fermions). The thermal average of the particle number, $\langle N \rangle$, is then interpreted as the occupancy probability (often just called occupancy) of the state.

6.1 Fermi-Dirac Distribution

In a real system consisting of a large number of fermions it is useful to focus on one state, call this the system $\mathcal{S}$, and think of all the other states as the reservoir. Our goal is to find the thermal average occupancy of the singled out state $\mathcal{S}$.

Recall that the Pauli exclusion principle says that "A state can only be occupied by 0 or 1 fermion". This means that our average occupancy will be between zero and 1.

The model of our system is the following, the state is either empty or contains a single free fermion. The quantity ε can be either the kinetic energy of the fermion or its spin orientation. We assume that the fermion is confined to a fixed volume[16], and that the fermion gas, e.g the system plus the reservoir, is either non- or weakly interacting.
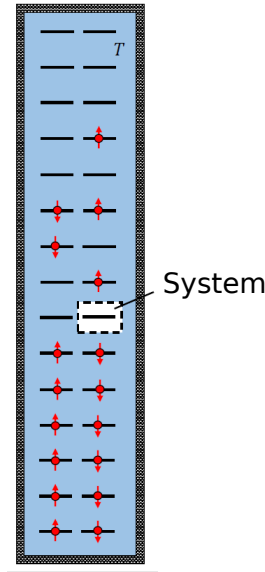
Figure 23: A model of a real gas of fermions, e.g. electrons in a metal. The system consists of one single-fermion state

By considering the two possibilities we can compute the grand partition function and hence the average occupation number.

1. When the state is unoccupied it has zero energy and the reservoir consists of N_0 fermions with energy U_0. The fundamental entropy for the total system (system + reservoir) is thus $\sigma(N_0, U_0) = \ln \Omega(N_0, U_0)$. This means that the unoccupied system has the Gibbs factor $e^0 = 1$.

2. If the state is occupied it has one fermion in it with energy ε. The reservoir thus consists of $N_0 - 1$ fermions and energy $U_0 - \varepsilon$. The fundamental entropy is thus $\sigma(N_0 - 1, U_0 - \varepsilon) = \ln \Omega(N_0 - 1, U_0 - \varepsilon)$, Taylor expanding we find that

$$\sigma(N_0 - 1, U_0 - \varepsilon) \simeq \sigma(N_0, U_0) + \beta\mu - \beta\varepsilon. \tag{6.1}$$

This results in the Gibbs factor of the occupied state being $e^{(\mu-\varepsilon)\beta}$.

---

[16]This is so we can use our understanding of the quantum mechanical particle in the box to compute the energy of the fermion.

Computing the grand partition function we thus have that

$$\mathcal{Z} = 1 + e^{(\mu - \varepsilon)\beta} = 1 + \lambda e^{-\beta\varepsilon}. \tag{6.2}$$

From the partition function we can compute the thermal average occupation number:

$$\langle N \rangle = \lambda \frac{\partial \ln \mathcal{Z}}{\partial \lambda} \tag{6.3}$$

$$= \lambda \frac{\partial}{\partial \lambda} \ln \left(1 + \lambda e^{-\beta\varepsilon}\right) \tag{6.4}$$

$$= \frac{\lambda e^{-\beta\varepsilon}}{\lambda e^{-\beta\varepsilon} + 1} \tag{6.5}$$

$$= \frac{1}{\lambda^{-1} e^{\beta\varepsilon} + 1}. \tag{6.6}$$

We call the thermal occupancy of a state with energy ε the distribution function:

$$f(\varepsilon) = \langle N(\varepsilon) \rangle = \frac{1}{\lambda^{-1} e^{\beta\varepsilon} + 1}. \tag{6.7}$$

Substituting in the fugacity we have the conventional expression for the Fermi-Dirac distribution function,

$$f_{FD}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}. \tag{6.8}$$

The Fermi-Dirac distribution gives the average number of fermions in a single state of energy ε. A consequence of the Pauli exclusion principle is that $0 \leq f(\varepsilon) \leq 1$.

In the context of solid state physics it is conventional to refer to the chemical potential of a gas of fermions as the Fermi level, ε_F. The Fermi level is usually temperature dependent, since the chemical potential is. At absolute zero the Fermi-level is called the Fermi-energy, $\varepsilon_{F0} = \mu(T = 0)$.

At $T = 0$ all states below the Fermi energy are occupied by exactly one fermion, all other states are unoccupied. For $T > 0$ the value of μ is no longer the Fermi energy. A state at the Fermi level $\varepsilon = \mu$ is half-filled ($f = \frac{1}{2}$) in the sense of the Fermi-Dirac distribution.

Need to add figures of $f(\varepsilon)$.

In a general Fermi gas we can introduce a reference temperature, known as the Fermi temperature, T_F, through $\varepsilon_{F0} = \kappa_B T_F$. Typically the Fermi temperature is close to $50000K$ for the free conduction electrons in a metal. The Fermi temperature is not a "real" temperature, it is a reference temperature corresponding to the Fermi energy. We then have the criteria

- If $T_F \gg T$: call the gas degenerate.

- If $T_F \ll T$: the gas is in the classical regime.

We can also introduce a velocity through $\varepsilon_{F0} = \frac{1}{2} m v_{F0}^2$.

	Conduction electron concentration $(\frac{N}{V})$	Fermi velocity	Fermi energy	Fermi Temperature
Li	$4.6 \times 10^{22} \text{cm}^{-3}$	$1.3 \times 10^{8} \text{cms}^{-1}$	4.7eV	$5.5 \times 10^{4} K$
Na	$2.5 \times 10^{22} \text{cm}^{-3}$	$1.1 \times 10^{8} \text{cms}^{-1}$	3.1eV	$3.7 \times 10^{4} K$
K	$1.34 \times 10^{22} \text{cm}^{-3}$	$0.85 \times 10^{8} \text{cms}^{-1}$	2.1eV	$2.4 \times 10^{4} K$
Rb	$1.08 \times 10^{22} \text{cm}^{-3}$	$0.79 \times 10^{8} \text{cms}^{-1}$	1.8eV	$2.1 \times 10^{4} K$
Cs	$0.86 \times 10^{22} \text{cm}^{-3}$	$0.73 \times 10^{8} \text{cms}^{-1}$	1.5eV	$1.8 \times 10^{4} K$
Cu	$8.5 \times 10^{22} \text{cm}^{-3}$	$1.56 \times 10^{8} \text{cms}^{-1}$	7.0eV	$8.2 \times 10^{4} K$
Ag	$5.76 \times 10^{22} \text{cm}^{-3}$	$1.38 \times 10^{8} \text{cms}^{-1}$	5.5eV	$6.4 \times 10^{4} K$
Au	$5.90 \times 10^{22} \text{cm}^{-3}$	$1.39 \times 10^{8} \text{cms}^{-1}$	5.5eV	$6.4 \times 10^{4} K$

Table 4: Examples of the Fermi quantities for a variety of metals. Taken from [KK80]. The units of ε_{F0} are electron volts, related to an energy in joules through, $1\text{eV} = 1.6 \times 10^{-19}$.

6.2   Bose-Einstein Distribution

Now we turn our attention to Bosons and consider the distribution function for a system of non-interacting, identical, bosons in thermal and diffusive contact with the reservoir. We follow the same approach as in the Fermi-Dirac case and single out a specific state of the Bose-gas to be treated as our system.

Let the energy of a single state be ε. If occupied by N particles the energy of the system is $N\varepsilon$. The grand partition function is then

$$\mathcal{Z} = \sum_{N=0}^{\infty} \lambda^{N} e^{-\beta N \varepsilon} = \sum_{N=0}^{\infty} \left(\lambda e^{-\beta \varepsilon} \right)^{N}, \tag{6.9}$$

letting $x = \lambda e^{-\beta \varepsilon} < 1$ this becomes a convergent geometric series with

$$\mathcal{Z} = \sum_{N=0}^{\infty} x^{N} = \frac{1}{1-x} = \frac{1}{1 - \lambda e^{-\beta \varepsilon}}. \tag{6.10}$$

The thermal average occupancy of the state is then

$$f(\varepsilon) = \langle N \rangle = \lambda \frac{\partial \ln \mathcal{Z}}{\partial \lambda} = -x \frac{d \ln \mathcal{Z}}{dx} = \frac{x}{1-x} = \frac{1}{\lambda^{-1} e^{\beta \varepsilon} - 1}, \tag{6.11}$$

this leads to the Bose-Einstein distribution

$$f_{BE}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1}. \tag{6.12}$$

This gives the thermal average of the number of bosons in a single state of energy ε.

6.3   Maxwell-Boltzmann Distribution and the Classical Limit

We can compare the two distributions, Equations (6.8) and (6.12), in the limit that the exponential factor is large, $e^{\beta(\varepsilon - \mu)} \gg 1$. In this limit the plus or minus one in the denominator is
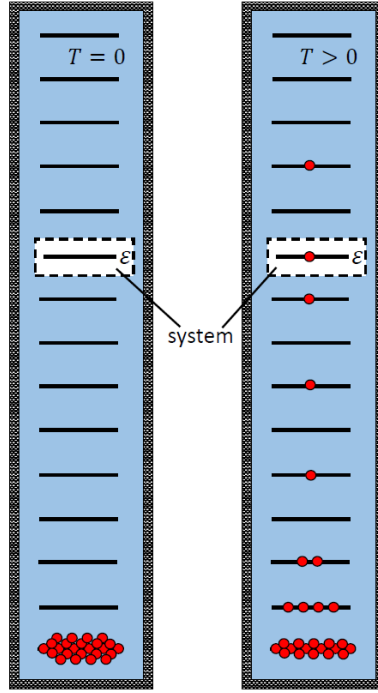
Figure 24: A model of a Bose-gas. On the left is $T = 0$ and on the right is $T > 0$.
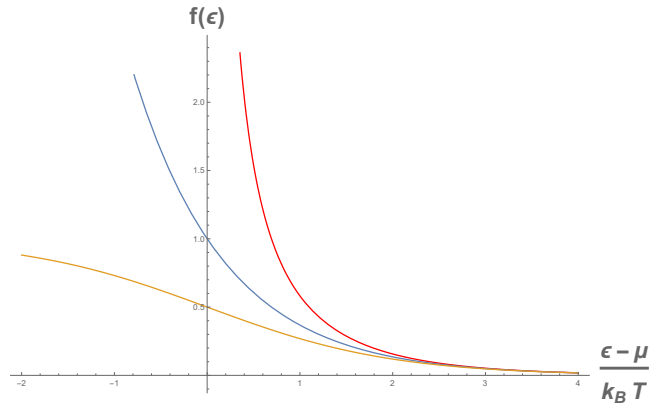
Figure 25: A comparison of the three distribution functions; $f_{BE}(\varepsilon)$ in red, $f_{FD}(\varepsilon)$ in orange, and $f_{MB}(\varepsilon)$ in blue. For large values of $\beta(\varepsilon - \mu)$ the three distributions agree.

negligible and $f(\varepsilon) \ll 1$, another way to say this is that there are more states available than particles to fill them. This means that for both Fermions and Bosons the limit of the thermal average occupancy of a state with energy ε is given by the Maxwell-Boltzmann distribution. The three distributions are compared in Figure 25.

The large $\beta(\varepsilon - \mu)$ limit results in the classical Maxwell-Boltzmann distribution

$$f_{MB}(\varepsilon) = \lambda e^{-\beta \varepsilon}. \tag{6.13}$$

This is the classical distribution function giving the average occupancy of one state with energy ε.

All particles are either fermions or bosons, they behave fundamentally differently in the quan-

tum regime but alike in the classical regime. In the classical regime the concentration, n, is small in comparison to the quantum concentration, n_q. Thus the classical regime is when $n \ll n_q = \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}$.

Regime	Type of particle	$f(\varepsilon)$
Classical	Boson	$\ll 1$
	Fermion	$\ll 1$
Quantum	Boson	State of lowest energy has $f(\varepsilon) \gg 1$
	Fermion	close to but less than 1

Table 5: A table comparing the distribution function for bosons and fermions in the the classical and quantum regimes.

We can now consider the classical limit. Generally we have that

$$N = \langle N \rangle = \sum_i f(\varepsilon_i), \tag{6.14}$$

for an identical monatomic gas in the classical regime this is given by

$$N = \lambda \sum_i e^{-\beta \varepsilon_i} = \lambda Z_1 = \lambda n_Q V. \tag{6.15}$$

This implies that the fugacity is given by

$$E^{\beta \mu} = \lambda = \frac{N}{n_q V} = \frac{n}{n_Q}. \tag{6.16}$$

Hence the chemical potential can be expressed as

$$\mu = \frac{1}{\beta} \ln\left(\frac{n}{n_Q}\right) = \frac{1}{\mu}\left[\ln N - \ln V + \frac{3}{2}\ln\beta + \ln\left(\frac{h^2}{2\pi m}\right)\right]. \tag{6.17}$$

Now from μ the thermodynamic quantities F, U, and S can be calculated. We can also derive the ideal gas law and expressions for the heat capacities. The free energy follows from integrating

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}, \tag{6.18}$$

and S, P follow from derivatives of F. By considering $U = F - TS$ we then find that

$$U = \frac{3}{2}N k_B T. \tag{6.19}$$

The energy, ε, is always defined within a constant , i.e. the zero of the energy is arbitrary, though there is often a natural choice. This choice will affect the value of the chemical potential, however, $\varepsilon - \mu$ is independent of the choice of zero for ε.

6.4 Fermi Gases, Density of states, and the Heat Capacity of an Electron Gas

Turning our attention back to the Fermi gas, recall that the quantum concentration is given by $n_Q = \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}$, this can be rearranged to give a temperature,

$$T_0 = n_Q^{\frac{2}{3}} \frac{2\pi \hbar^2}{m k_B} \tag{6.20}$$

with $\hbar = \frac{h}{2\pi}$ the reduced version of Planck's constant. A Fermi gas in the quantum regime is called *degenerate* when the temperature is much lower than T_0, $T \ll T_0$.

The free electron model of metals is the prototypical example of a Fermi gas. Studying the electron states of this Fermi gas gives insights into the electrical and magnetic properties of conductors, as well as the electron contribution to the heat capacity.

The assumptions in the free electron model are:

1. Valence electrons are fully detached from the ionic rest atoms.

2. The wave function of an electron extends over many atoms.

3. The electrons do not interact with each other or with the ions.

4. There are infinite potential energy barriers at the surfaces of the conductor.

Armed with these assumptions we can model an electron as a quantum mechanical particle in a box. For an electron in a cubic box with side length L, volume $V = L^3$, the wave function and energy levels are given by Equations (4.6) and (4.7):

$$\psi_{n_x,n_y,n_z}(x, y, z) = c \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right),$$

$$\varepsilon_{n_x,n_y,n_z} = \frac{\left(n_x^2 + n_y^2 + n_z^2\right) \pi^2 \hbar^2}{2mL^2},$$

with the quantum numbers n_x, n_y, n_z being positive integers $(1, 2, 3, \dots)$. Sometimes the energy will be written in terms of a wavevector $\vec{k} = \frac{\pi}{L}(n_x, n_y, n_z)$.

The *density of states*,

$$\mathcal{D}(\varepsilon) = \frac{dn}{d\varepsilon}, \tag{6.21}$$

is the number of states, dn, in the energy $(\varepsilon, \varepsilon + d\varepsilon)$. To understand[17] it consider a three dimensional space with coordinates (n_x, n_y, n_z). A surface of constant energy ε_r (the largest energy level) is given by the sphere of radius $n_r^2 = n_x^2 + n_y^2 + n_z^2$. We are interested in the density of states within the positive octant, as the quantum numbers are all positive $n_x, n_y, n_z > 0$. The total ball has a volume of $V = \frac{4}{3}\pi n_r^3$, so the positive octant has a volume of

$$V_{\text{Oct}} = \frac{1}{8} V_B = \frac{1}{8} \frac{4}{3} \pi n_r^3 = \frac{\pi}{6} n_r^3. \tag{6.22}$$

---

[17]For discrete quantities the density will be the number of states divided by the volume the states fill in state space, e.g. the space of allowed quantum numbers.

Since electrons have spin $\frac{1}{2}$ there are two electron states for every point (n_x, n_y, n_z), these correspond to the electron being spin up or spin down, $m_s = \pm\frac{1}{2}$. Thinking of the quantum numbers as being continuous, the number of electron states in the positive octant is

$$n = 2 \times V_{\text{Oct}} = \frac{\pi}{3} n_r^3, \tag{6.23}$$

which we can solve for the radius of the sphere as $n_r = \left(\frac{3n}{\pi}\right)^{\frac{1}{3}}$. Note that here n is the number of states within the ball **not** the number density as it was in the last section. We can thus express the energy at the surface of the sphere as a function of the number of states as

$$\varepsilon = \frac{n_r^2 \pi^2 \hbar^2}{2mL^2} = \frac{\left(\frac{3n}{\pi}\right)^{\frac{2}{3}} \pi^2 \hbar^2}{2mL^2}, \tag{6.24}$$

expanding an rearranging gives the number of states within the ball of energy ε is

$$n(\varepsilon) = \frac{(2m)^{\frac{3}{2}} V \varepsilon^{\frac{3}{2}}}{3\pi^2 \hbar^3}. \tag{6.25}$$

Differentiating this gives the density of state,

$$\mathcal{D}(\varepsilon) = \frac{dn}{d\varepsilon} = \frac{(2m)^{\frac{3}{2}} V}{2\pi^2 \hbar^3} \varepsilon^{\frac{1}{2}}. \tag{6.26}$$

The density of states depends on the dimension, on the problem sheets you will compute the two-dimensional density of states.

Recall that the probability that a specific state with energy ε is occupied at temperature T is $f(\varepsilon, T, \mu)$. To find the number of electrons, dN, in the energy range $(\varepsilon, \varepsilon + d\varepsilon)$ this probability needs to be multiplied by the density of states,

$$dN = f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon. \tag{6.27}$$

Upon integration over the energy we find the total number of electrons in the electron gas:

$$N = \int_0^\infty f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon. \tag{6.28}$$

The internal energy (total kinetic energy) of the electron gas follows from $dU = \varepsilon dN$:

$$U = \int_0^\infty \varepsilon f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon. \tag{6.29}$$

At absolute zero, $T = 0$, these expressions simplify as the Fermi-Dirac distribution is a step function

$$f(\varepsilon) = \begin{cases} 1 & \varepsilon < \varepsilon_{F0} \\ 0 & \varepsilon > \varepsilon_{F0}. \end{cases} \tag{6.30}$$

The particle number from Equation (6.28) can now be evaluated as

$$N = \int_0^{\varepsilon_{F0}} 1 \mathcal{D}(\varepsilon)d\varepsilon + \int_{\varepsilon_{F0}}^{\infty} (0)\,\mathcal{D}(\varepsilon)d\varepsilon \tag{6.31}$$

$$= \int_0^{\varepsilon_{F0}} \mathcal{D}(\varepsilon)d\varepsilon \tag{6.32}$$

$$= \frac{(2m)^{\frac{3}{2}} V \varepsilon_{F0}^{\frac{3}{2}}}{3\pi^2 \hbar^3}. \tag{6.33}$$

Rearranging this we find that the Fermi energy of the electron gas is

$$\varepsilon_{F0} = \frac{3^{\frac{2}{3}} \pi^{\frac{4}{3}} \hbar^2}{2m} \left(\frac{N}{V}\right)^{\frac{2}{3}}, \tag{6.34}$$

here $\frac{N}{V}$ is the number density of electrons in the gas, also known as the conduction electron concentration. This calculation shows how the Fermi-energy is computed in three dimensions, to find it for an electron gas in any other direction the same sort of calculation is done using the appropriate density of states.

The total ground state energy is then given by

$$U_0 = \int_0^{\varepsilon_{F0}} \varepsilon \mathcal{D}(\varepsilon)d\varepsilon. \tag{6.35}$$

Using the expression for the total particle number the density of states can be expressed as

$$\mathcal{D}(\varepsilon) = \frac{3}{2} \frac{N}{\varepsilon_{F0}^{\frac{3}{2}}} \varepsilon^{\frac{1}{2}}. \tag{6.36}$$

Making use of this new expression the integral for U can be carried out to find

$$U_0 = \frac{3N}{2\varepsilon_{F0}^{\frac{3}{2}}} \int_0^{\varepsilon_{F0}} \varepsilon^{\frac{3}{2}} d\varepsilon = \frac{3}{5} N \varepsilon_{F0}, \tag{6.37}$$

so the average energy per electron, $\frac{U}{N}$, at $T = 0$ is $\frac{3}{5}\varepsilon_{F0}$.

Turning our attention to systems at non zero temperature, it is natural to ask what the increase in energy is when a system of N electrons is heated from $0K$ to a temperature T:

$$\Delta U = U(T) - U_0 = \int_0^{\infty} \varepsilon f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon - \int_0^{\varepsilon_{F0}} \varepsilon \mathcal{D}(\varepsilon)d\varepsilon. \tag{6.38}$$

The total particle number of the electron gas is not changing as we heat the gas so we can still write

$$N = \int_0^{\varepsilon_{F0}} \mathcal{D}(\varepsilon)d\varepsilon = \int_0^{\infty} f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon, \tag{6.39}$$

multiplying by the Fermi-energy we have that

$$\int_0^{\varepsilon_{F0}} \varepsilon_{F0}\mathcal{D}(\varepsilon)d\varepsilon = \int_0^{\varepsilon_{F0}} \varepsilon_{F0}f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon, + \int_{\varepsilon_{F0}}^{\infty} \varepsilon_{F0}f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon. \tag{6.40}$$

The identity in Equation (6.40) can be used to add zero to ΔU and express it as

$$\Delta U = \int_{\varepsilon_{F0}}^{\infty} (\varepsilon - \varepsilon_{F0})\, f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon \quad + \int_{0}^{\varepsilon_{F0}} (\varepsilon_{F0} - \varepsilon)\left[1 - f(\varepsilon)\right]\mathcal{D}(\varepsilon)d\varepsilon, \qquad (6.41)$$

the two terms in this expression can be understood as follows:

1. The first term is the energy needed to take an electron with energy ε_{F0} and raise it to a state with energy above the Fermi energy $\varepsilon > \varepsilon_{F0}$.

2. The second terms is the energy needed to bring an electron from a state below the Fermi energy to a state at the Fermi energy.

In other words it describes how the energy of electrons are increased during the heating.

At constant volume when heat is added to a system the specific heat capacity is defined as

$$C_V = \left(\frac{dQ}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V. \qquad (6.42)$$

To compute the heat capacity we need to differentiate ΔU with respect to temperature. To facilitate this expand ΔU to

$$\Delta U = \int_{\varepsilon_{F0}}^{\infty} (\varepsilon - \varepsilon_{F0})\, f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon + \int_{0}^{\varepsilon_{F0}} (\varepsilon_{F0} - \varepsilon)\,\mathcal{D}(\varepsilon)d\varepsilon$$
$$+ \int_{0}^{\varepsilon_{F0}} (\varepsilon - \varepsilon_{F0})\, f(\varepsilon)\mathcal{D}(\varepsilon)d\varepsilon. \qquad (6.43)$$

All of the temperature dependence is in the Fermi-Dirac distribution, so the second term does not contribute to the derivative. We thus have that

$$\frac{dU}{dT} = \int_{\varepsilon_{F0}}^{\infty} (\varepsilon - \varepsilon_{F0})\frac{df(\varepsilon)}{dT}\mathcal{D}(\varepsilon)d\varepsilon + \int_{0}^{\varepsilon_{F0}} (\varepsilon - \varepsilon_{F0})\frac{df(\varepsilon)}{dT}\mathcal{D}(\varepsilon)d\varepsilon \qquad (6.44)$$

$$= \int_{0}^{\infty} (\varepsilon - \varepsilon_{F0})\frac{df(\varepsilon)}{dT}\mathcal{D}(\varepsilon)d\varepsilon. \qquad (6.45)$$

The heat capacity is

$$C_V = \int_{0}^{\infty} (\varepsilon - \varepsilon_{F0})\frac{df(\varepsilon)}{dT}\mathcal{D}(\varepsilon)d\varepsilon. \qquad (6.46)$$

This expression is not explicit, to improve it we need to evaluate $\frac{df(\varepsilon)}{dT}$. Fortunately, for $T \ll T_F$ we can use that $\frac{df(\varepsilon)}{dT}$ is only significant near the Fermi energy, $\varepsilon \simeq \varepsilon_{F0}$, we can read this off the plots, $\frac{df(\varepsilon)}{dT}$ is sharply peaked around the Fermi level and becomes a delta function in the $T \to 0$ limit. In other words when $T \ll T_F$ we can ignore the temperature dependence of μ, in [Man71] an approximate expression for μ as a function of T is found and it is ε_{F0} with a correction term depending on $\left(\frac{T}{T_F}\right)^2$. We can thus replace $\mathcal{D}(\varepsilon)$ by $\mathcal{D}(\varepsilon_{F0})$, giving the electron heat capacity as

$$C_{\mathrm{el}} \simeq \mathcal{D}(\varepsilon_{F0}) \int_{0}^{\infty} (\varepsilon - \varepsilon_{F0})\frac{df(\varepsilon)}{dT}d\varepsilon. \qquad (6.47)$$

to make further progress we need to compute $\frac{df(\varepsilon)}{dT}$ for $\varepsilon_F \simeq \varepsilon_{F0}$:

$$\frac{df(\varepsilon)}{dT} = \frac{d}{dT}\left[\frac{1}{\exp\left(\frac{\varepsilon-\varepsilon_{F0}}{k_B T}\right)+1}\right] \tag{6.48}$$

$$= -\frac{1}{\left(\exp\left(\frac{\varepsilon-\varepsilon_{F0}}{k_B T}\right)+1\right)^2}\exp\left(\frac{\varepsilon-\varepsilon_{F0}}{k_B T}\right)\left(-\frac{(\varepsilon-\varepsilon_{F0})}{k_B T^2}\right). \tag{6.49}$$

Next let $x(\varepsilon) = \frac{\varepsilon-\varepsilon_{F0}}{k_B T}$ so that $x(0) = -\frac{\varepsilon_{F0}}{k_B T}$ and $dx = \frac{d\varepsilon}{k_B T}$ so that $x^2 = \frac{(\varepsilon-\varepsilon_{F0})^2}{k_B k_B T^2}$ and the electron heat capacity becomes

$$C_{\text{el}} \simeq k_B^2 T \mathcal{D}(\varepsilon_{F0}) \int_{-\frac{\varepsilon_{F0}}{k_B T}}^{\infty} \frac{x^2 e^x}{(e^x+1)^2}dx. \tag{6.50}$$

The lower limit can be replaced by $-\infty$ as e^x is already negligible for $\frac{\varepsilon_{F0}}{k_B T} \sim 100$, e.g. at low temperatures.

The integral is then evaluated as

$$\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2}dx = \frac{\pi^2}{3}, \tag{6.51}$$

giving

$$C_{\text{el}} \simeq k_B^2 T \mathcal{D}(\varepsilon_{F0})\frac{\pi^2}{3} = \frac{1}{3}\pi^2 k_B^2 T \mathcal{D}(\varepsilon_{F0}). \tag{6.52}$$

Substituting in the density of states, $\mathcal{D}(\varepsilon_{F0}) = \frac{3}{2}\frac{N}{\varepsilon_{F0}^{\frac{3}{2}}}\varepsilon_{F0}^{\frac{1}{2}} = \frac{3N}{2k_B T_F}$, to get

$$C_{\text{el}} \simeq \frac{\pi^2}{2}Nk_B\frac{T}{T_F} \qquad \text{when } T \ll T_F. \tag{6.53}$$

The electron contribution to the heat capacity is thus linear in temperature. Recall that the Fermi-temperature is not a real temperature, rather it is a reference point. As T_F is typically around $50000K$ in ordinary metals the condition that $T \ll T_F$ is satisfied in ordinary metals near room temperature.

The overall heat capacity of metals is given by the sum of the electron contribution (C_{el}) and the lattice vibration (phonon) contribution[18]

$$C_V = C_{\text{el}} + C_{\text{ph}}. \tag{6.54}$$

At low temperatures ($T \ll \Theta$ the Debye temperature) this is

$$C_V = \gamma T + AT^3, \tag{6.55}$$

---

[18]We may return to this result later.

with

$$\gamma = \frac{\pi^2}{2} \frac{N k_B}{T_F}, \tag{6.56}$$

$$A = \frac{12\pi^4}{5} \frac{N_{\text{at}} k_B}{\Theta^3}, \tag{6.57}$$

$$\Theta = \left(\frac{\hbar c_{\text{sound}}}{k_B} \right) \left(\frac{6\pi^2 N_{\text{at}}}{V} \right)^{\frac{1}{3}}, \tag{6.58}$$

with N_{at} the number of atoms. Equation (6.56) is known as the Sommerfeld coefficient and has units of JK^{-2}.

The cubic dependence of C_V on T is called the Debye T^3-law for the Heat capacity of solids. We may return to discuss this in more detail later in in the module.

The model for the specific heat capacity of metals depends on both forms of quantum statistics:

- The Debye model treats the vibrations of the atomic lattice as phonons in a box, these obey Bose-Einstein statistics

- The heat capacity of conduction electrons is based on Fermi-Dirac statistics.

The electron contribution to the heat capacity is only significant at very low temperatures and dominates in the $T \to 0K$ limit. e.g. in monovalent metals $\frac{\gamma}{A} \simeq 0.02 \frac{\theta^3}{T_F}$ is of order 1.

For example: $Li \frac{\gamma}{A} = 14.8K^2$, $Na \frac{\gamma}{A} = 2.1K^2$, $K \frac{\gamma}{A} = 0.6K^2$, $Rb \frac{\gamma}{A} = 0.2K^2$, $Cs \frac{\gamma}{A} = 0.06K^2$, $Cu \frac{\gamma}{A} = 9.8K^2$, $Ag \frac{\gamma}{A} = 3.6K^2$, and $Au \frac{\gamma}{A} = 1.4K^2$.

Finally we give an example of how to compute the pressure for a Fermi gas at absolute zero.

Example 6.1. Pressure in a Fermi gas at $T = 0$
Consider the Helmholtz free energy of a Fermi gas at absolute zero,

$$F(T = 0) = (E - TS)_{T=0} = E_0, \tag{6.59}$$

where by the third law $S = 0$ at $T = 0$, and E_0 is the energy of the Fermi gas at absolute zero.

Because of the Pauli exclusion principle the states are all filled upto the Fermi energy, ε_{F0}. We computed previously that the energy at $T = 0$ is given by

$$E_0 = \frac{3}{5} N \varepsilon_{F0}, \tag{6.60}$$

the free energy is thus given by the same expression

$$F(T = 0) = \frac{3}{5} N \varepsilon_{F0} = \frac{3}{10} N \frac{\hbar^2 \left(3\pi^2 \right)^{\frac{1}{3}}}{m} \left(\frac{N}{V} \right)^{\frac{2}{3}}, \tag{6.61}$$

where we have made use of the Fermi energy from Equation (6.34). The pressure is then found from the thermodynamic relation

$$p = - \left(\frac{\partial F}{\partial V} \right)_T. \tag{6.62}$$

Computing this derivative gives

$$p(T = 0) = \frac{1}{5} \frac{\hbar^2 (3\pi^2)^{\frac{1}{3}}}{m} \left(\frac{N}{V}\right)^{\frac{5}{3}}. \qquad (6.63)$$

There is thus a finite, non zero pressure in a Fermi gas even at $T = 0$. This pressure depends on the number density of the gas, $\frac{N}{V}$, and is often called the *fermion degeneracy pressure*. The non zero temperature version of this pressure is responsible for supporting both white dwarfs (electron degeneracy pressure) and neutron stars (neutron degeneracy pressure) against gravitational collapse.

6.5   The Bose Gas and Bose-Einstein Condensation

For the Bose gas the distribution function is

$$f_{BE}(\varepsilon, T) = \frac{1}{e^{\frac{\varepsilon - \mu}{k_B T}} - 1}. \qquad (6.64)$$

For the lowest energy state $\varepsilon = 0$ this becomes $f_{BE}(0, T) = \frac{1}{e^{\frac{-\mu}{k_B T}} - 1}$. In the low temperature $(T \to 0)$ limit all the particles are in the ground state. The low temperature limit of the distribution function is then

$$N = \lim_{T \to 0} f_{BE}(0, T) = \lim_{T \to 0} \frac{1}{e^{\frac{-\mu}{k_B T}} - 1} \simeq \frac{1}{1 - \frac{\mu}{k_B T} - 1} \simeq -\frac{k_B T}{\mu}. \qquad (6.65)$$

So as the temperature goes to zero the chemical potential is given in terms of the number of particles as

$$N = -\frac{k_B T}{\mu}, \qquad \text{and} \quad \mu = -\frac{k_B T}{N}. \qquad (6.66)$$

The fugacity is also related to the particle number,

$$\lim_{T \to 0} \lambda = \lim_{T \to 0} e^{\frac{\mu}{k_B T}} \simeq 1 - \frac{1}{N}. \qquad (6.67)$$

Generally the chemical potential can be thought of as saying how accepting the system is of new particles, e.g. how much work needs to be done to add a new particle to the system.

- For bosons $\mu \leq 0$.

- For fermions $\mu > 0$.

We will see later that for both photons and phonons the chemical potential is zero.

For example in Helium 4 with $N = 10^{22}$ at $T = 1K$ the chemical potential is $\mu \simeq -1.4 \times 10^{-45} J$.

Consider the energy levels of a particle in a box, Figure 12, the gap between the first excited state and the lowest energy state is

$$\Delta \varepsilon = \frac{3\pi^2 \hbar^2}{2mL^2}. \qquad (6.68)$$

Focusing on Helium 4, with the mass of an atom being $m = 6.6 \times 10^{-27} Kg$, in a cube of side length $L = 1cm$ we have that $\Delta\varepsilon = 2.5 \times 10^{-37}$ and

$$\frac{\Delta\varepsilon}{k_B} = 1.8 \times 10^{-14} K. \tag{6.69}$$

The expected occupation number of the first excited state at $T = 10^{-3}K$ is given by the Boltzmann factor, $e^{-\Delta\varepsilon\beta} = \exp{-1.8 \times 10^{-11}} \simeq 1 - 1.8 \times 10^{-11} \simeq 1$, even when the concentration is of the order of the quantum concentration, $n \simeq n_Q$.

However, the Bose-Einstein distribution gives a very different value for the occupancy of $\varepsilon_{2,1,1}$ at $T = 10^{-3}K$:

$$\mu = -\frac{k_B T}{N} = -\frac{10^{-3} k_B}{10^{22}} = -1.4 \times 10^{-48} J, \tag{6.70}$$

for N the total number of particles in the system. Thus $\mu \ll \Delta\varepsilon$ and the distribution function is

$$f_{BE}(\Delta\varepsilon, T) = \left(\exp\left(\frac{\Delta\varepsilon - \mu}{k_B T}\right) - 1\right)^{-1} \simeq \left(\exp\left(\frac{\Delta\varepsilon}{k_B T}\right) - 1\right)^{-1} = 5 \times 10^{10}, \tag{6.71}$$

so $\frac{f}{N} \simeq 5 \times 10^{-12} \ll 1$. Thus only a tiny fraction of the particles are in the first excited state. The occupancy of the first excited state is thus much lower than we would expect by just looking at the Boltzmann factor. At sufficiently low temperatures the Bose-Einstein distribution function favours a situation where the majority of particles are in the ground state. The particles in the ground state, as long as there number $N_0 \gg 1$, are called a Bose-Einstein condensate[19].

At low temperatures the chemical potential is much closer to the ground state energy, $\varepsilon_{1,1,1}$ conventionally set to zero, than to the energy of the first excited state, $\varepsilon_{2,1,1}$. This "closeness" of μ to $\varepsilon_{1,1,1}$ means that most of the population of the system is in the ground state.

The density of states for a gas of massive[20] bosons is

$$\mathcal{D}(\varepsilon) = \frac{(2m)^{\frac{3}{2}} V}{4\pi^2 \hbar^3} \varepsilon^{\frac{1}{2}}. \tag{6.72}$$

The total particle number is given by

$$N = \sum_n f_n = N_0(T) + n_e(T) = N_0(T) + \int_0^\infty \mathcal{D}(\varepsilon) f(\varepsilon, T) d\varepsilon, \tag{6.73}$$

here the sum over the distribution function has been split in to two pieces, the ground state population, and the sum over all of the excited states. The integral only gives the total occupation of the excited states since the density of states vanishes for $\varepsilon = 0$, $\mathcal{D}(0) = 0$.

Some examples of the Bose-Einstein distribution function for large particle number[21] at low temperatures are given in Figure 26

---

[19]As they are all in the same state we have a "macroscopic" number of particles governed by a single quantum wavefunction.

[20]For massless bosons like photons and phonons the density of states is slightly different, we will encounter that soon.

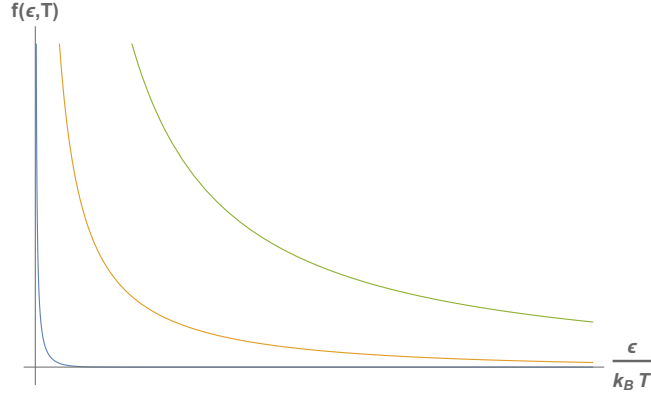[21]large N so that $\lambda \simeq 1$ and $\mu \simeq 0$.

Figure 26: Plots of the Bose-Einstein distribution at three different temperatures; blue $k_B T = 0.1J$, orange $k_B T = 0.5J$, and green $k_B T = 1J$.

Sometimes we refer to $N_0(T)$ as the condensate occupancy and $N_e(T)$ as the "normal phase" occupancy. This is because the Bose-Einstein condensate is in a superfluid phase. For low temperatures and large particle number we can express the occupancies as

$$N_0(T) = \frac{1}{\lambda^{-1} - 1} = \left(e^{\frac{-\mu}{k_B T}} - 1\right)^{-1}, \tag{6.74}$$

$$N_e(T) = \int_0^\infty \mathcal{D}(\varepsilon) f(\varepsilon, T) d\varepsilon = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar}\right)^{\frac{3}{2}} \int_0^\infty \frac{\varepsilon^{\frac{1}{2}}}{\lambda^{-1} e^{\frac{\varepsilon}{k_B T}} - 1} d\varepsilon. \tag{6.75}$$

As $\lambda \simeq 1$ the integral in the normal phase occupancy can be evaluated using the substitution $k_B T x = \varepsilon$,

$$\int_0^\infty \frac{\varepsilon^{\frac{1}{2}}}{\lambda^{-1} e^{\frac{\varepsilon}{k_B T}} - 1} d\varepsilon = (k_B T)^{\frac{3}{2}} \int_0^\infty \frac{x^{\frac{1}{2}}}{e^x - 1} dx = 1.306 \pi^{\frac{1}{2}} (k_B T)^{\frac{3}{2}}. \tag{6.76}$$

Substituting Equation (6.76) into Equation (6.75), and recalling the formula for the quantum concentration, n_Q, we find

$$N_e(T) = 2.612 V n_Q. \tag{6.77}$$

Thus as a fraction of the total particle number the occupation of the normal phase is

$$\frac{N_e}{N} = 2.612 \frac{n_Q V}{N} = 2.612 \frac{n_Q}{n}. \tag{6.78}$$

For a system with a "large enough" N_0 to have a condensate the Einstein condensation temperature, T_e is defined as

$$T_e = \frac{2\pi \hbar^2}{m k_B} \left(\frac{N}{2.612 V}\right)^{\frac{2}{3}}, \tag{6.79}$$

so that

$$\frac{N_e}{N} \simeq \left(\frac{T}{T_e}\right)^{\frac{3}{2}}, \tag{6.80}$$

and the occupation of the excited states varies as $T^{\frac{3}{2}}$ for $T < T_e$. For Helium 4 the value of T_e is $3.1K$. At the Einstein condensation temperature all the particles are in the normal phase,

$$N_e(T_e) = N. \tag{6.81}$$

53

Thus the condensate only exists for temperatures below T_e. For $T < T_e$, but close to T_e, a large number of particles are in the ground state, the Bose gas is said to be in the condensed (or superfluid) phase.

Include some more plots.

6.6 Phonons and the Debye Law.

This section will include a derivation of the Debye law for the phonon contribution to the heat capacity of solids. See Chapter 4, page 104 of [KK80] for more details. The key idea is to treat the lattice atoms as coupled oscillators.

6.6.1 The Planck Distribution

The spectrum of lattice vibrations and the spectrum of black body radiation are described by the Planck distribution. In both cases the associated quantum particles are massless bosons, phonons and photons respectively.

For atoms in a lattice (e.g the atoms making up a metal) model the vibrational degrees of freedom using harmonic oscillators[22]. A vibration of frequency ω_n corresponds to a state with energy $\varepsilon_n = \hbar\omega_n$, where again the zero point energy has been set to zero. We call these vibrations modes, they are n quanta[23] states with energy $\varepsilon_n = n\hbar\omega$.

The partition function in the grand canonical ensemble is

$$\mathcal{Z} = \sum_{n=0}^{n_D} e^{-n\hbar\omega\beta}, \tag{6.82}$$

there is no explicit sum over states since each particle is in a state with energy $\hbar\omega$. The limit n_D accounts for the fact that there is a maximum frequency of vibration, e.g. a maximum number of phonons. As for the Bose-Einstein distribution, let $x = e^{-\hbar\omega\beta} < 1$ so that the partition function is a convergent geometric series,

$$\mathcal{Z} = \sum_{n=0}^{n_D} x^n = \frac{1}{1-x} = \frac{1}{1 - e^{\hbar\omega\beta}}. \tag{6.83}$$

The probability that the system is in a state with n quanta is thus

$$p(n) = \frac{e^{-n\hbar\omega\beta}}{\mathcal{Z}}, \tag{6.84}$$

and the thermal average of the number of phonons is

$$\langle n \rangle = \sum_{0}^{n_D} np(n) = \sum_{0}^{n_D} n\frac{e^{-n\hbar\omega\beta}}{\mathcal{Z}}. \tag{6.85}$$

---

[22]It is natural to ask how valid modelling vibrating atoms as linear oscillators is. This is a good question to think about and depends on the material. In practice the linear approximation is enough.

[23]We use quanta rather than particle to avoid confusing the phonons with the atoms in the lattice. The lattices is vibrating, and these vibrations have frequencies which are integer multiples of a given frequency ω found by solving a quantum mechanical problem. The vibration with frequency ω is our quanta, called a phonon, or phonon mode, in a lattice.

We can evaluate this in terms of the y derivative of $\ln \mathcal{Z}$ with $y = \hbar\omega\beta$:

$$\langle n \rangle = \frac{d}{dy} \ln \mathcal{Z} = \frac{d}{dy} \ln \left(\frac{1}{1 - e^{-y}} \right) = \frac{1}{e^{\hbar\omega\beta} - 1}. \tag{6.86}$$

This is known as the Planck distribution and agrees with the Bose-Einstein distribution when the chemical potential is zero, $f(\varepsilon = \hbar\omega, \mu = 0)$.

The frequency of the mode is found by solving a particle in a box problem, $\omega_n = n c_{\text{sound}} \frac{\pi}{L}$. As the lattice is three dimensional $n^2 = n_x^2 + n_y^2 + n_z^2$ is given in terms of the three quantum numbers. Each atom has three modes associated with it, one for each direction that it can vibrate in.

Studying phonons leads to the Debye T^3- law that we encountered earlier when discussing the heat capacity of metals.

The thermal average of the energy for a gas of phonons is

$$U = \langle \varepsilon \rangle = \sum_n^{n_D} \varepsilon_n \frac{1}{e^{\hbar\omega_n\beta} - 1} = \sum_n^{n_D} \frac{\hbar\omega_n}{e^{\hbar\omega_n\beta} - 1}. \tag{6.87}$$

To evaluate this wee either need to find the phonon density of states[24] or by reasoning half-way to the density of states and then evaluating the integral. We will take the short cut first and return to give the density of states at the end.

In state space (the three dimensional space with coordinates n_x, n_y, n_z) the accessible states lie in a positive octant with radius n_D, the maximum quantum number. The volume of the positive octant is

$$V_{\text{oct}} = \frac{1}{6} \pi n_D^3, \tag{6.88}$$

there are three states per point for a total of $\frac{1}{2} \pi n_D^3$ states in the positive octant. The volume element is found by differentiating the expression for the volume, $dV = \frac{1}{2} \pi n^2 dn$. Thus the continuum limit is

$$\sum_{n=0}^{n_D} (\cdots) \to 3 \int_0^{n_D} dV (\cdots) = \frac{3\pi}{2} \int_0^{n_D} n^2 dn (\cdots). \tag{6.89}$$

The total energy becomes

$$U = \sum_n^{n_D} \frac{\hbar\omega_n}{e^{\hbar\omega_n\beta} - 1} = \frac{3\pi}{2} \int_0^{n_D} n^2 dn \frac{n\hbar\omega}{e^{n\hbar\omega\beta} - 1} \tag{6.90}$$

$$= \frac{3\pi}{2} \frac{1}{\hbar^3 \omega^3 \beta^4} \int_0^{y_D} \frac{y^3}{e^y - 1} dy, \quad \text{where } y = n\hbar\omega\beta. \tag{6.91}$$

The upper limit of the integral is

$$y_D = \hbar\omega\beta n_D = \hbar\beta \left(\frac{6 N \pi^2 c_{\text{sound}}^3}{V} \right)^{\frac{1}{3}} = k_B \Theta \beta, \tag{6.92}$$

---

[24]This is slightly trickier than finding the density of states for massive particles, as the expression for the energy of the system, $\varepsilon = n\hbar\omega$, is linear for phonons.

where we have used that $\omega = \frac{\pi c_{\text{sound}}}{L}$ and Θ is the Debye temperature. For $T \ll \Theta$ the upper limit y_D becomes very large and we take the upper limit of the integral to be ∞. The energy then becomes

$$U = \frac{3\pi\hbar\omega}{2} \frac{1}{(\hbar\omega\beta)^4} \int_0^\infty \frac{y^3}{e^y - 1} dy = \frac{3\pi\hbar\omega}{2} \frac{1}{(\hbar\omega\beta)^4} \frac{\pi^4}{15}, \quad (6.93)$$

where we make use of the standard integral

$$\int_0^\infty \frac{y^3}{e^y - 1} dy = \frac{\pi^4}{15}. \quad (6.94)$$

Making use of the Debye temperature and the expression for ω in terms of the speed of sound gives

$$U = \frac{3}{5}\pi^4 \frac{N}{(k_B\Theta)^3 \beta^4} \qquad \text{for } T \ll \Theta. \quad (6.95)$$

The heat capacity is given by the temperature derivative of the internal energy

$$C_V = \frac{dU}{dT} = \frac{12}{5}\pi^4 N k_B \left(\frac{T}{\Theta}\right)^3, \quad (6.96)$$

this is the Debye T^3-law that we encountered earlier.

We close this section by discussing the phonon density of states. For massive bosons and fermions the energy of a particle in the box is given by

$$\varepsilon = \frac{\pi^2\hbar^2 n^2}{2mL^2}. \quad (6.97)$$

However, for photons and phonons the energy is linear

$$\varepsilon = \hbar\omega, \quad (6.98)$$

for a single mode. To find the density of states it is easiest to work with the wave vector $k = \frac{\pi}{L}n$ which is related to the angular frequency through $\omega = k c_{\text{sound}}$. The density of states is defined such that integrating $\mathcal{D}(\varepsilon)d\varepsilon$ gives the total number of states, thus

$$\mathcal{D}(\varepsilon)d\varepsilon = \mathcal{D}(k)dk = 3dV = \frac{3}{2}\pi n^2 dn = \frac{3}{2}\pi k^2 dk \left(\frac{L}{\pi}\right)^3 = \frac{3V}{2\pi^2}k^2 dk = \frac{3V}{2\pi^2}\frac{\varepsilon^2}{(\hbar c_{\text{sound}})^3}d\varepsilon. \quad (6.99)$$

For phonons and photons, sometimes the density of states in written in terms of the frequency as

$$\mathcal{D}(\omega) = \frac{3V}{2\pi^2}\frac{\omega^2}{c_{\text{sound}}^3}d\omega. \quad (6.100)$$

Explaining this a bit more, previously we thought of the density of states as the number of states, dn, within the energy range, $(\varepsilon, \varepsilon + d\varepsilon)$. An equivalent way to think about this is to label the states within a range of wave numbers, $(k, k + dk)$. However, the density of wave numbers follows from the volume of the positive octant divide by the conversion factor between wave numbers and states.

6.7 *Quasi-particles and Superfluidity in Helium Four.

Superfluidity and the excitations that occur within the superfluid phase are discussed in [LLP80] and [Fey98]. However, these books make use of more advanced methods than we have in the course. The study of superfluidity is intrinsically quantum mechanical, in fact as you are quantising a classical field theory it is within the remit of quantum field theory. This intersection of statistical physics and quantum field theory is called *statistical field theory*.

The condensation temperature for Helium four of $T_e = 3K$ found above is suggestively close to the superfluid transition temperature of $2.17K$. The superfluid phase is related to the phenomena of Bose-Einstein condensation. ^{4}He becomes as liquid at $4.2K$, inter-atomic forces are relevant in a liquid so it is not modelled by a Bose gas. However, the inter-atomic forces responsible for the liquification are evidently not strong enough to stop condensation, just delay it to the lower temperature of $2.17K$. In other words for temperatures below $2.17K$ ^{4}He behaves like a gas of bosons.

There is also a superfluid phase in ^{3}He. However, this is a more subtle phenomena as ^{3}He atoms are fermions. They need to form Cooper pairs[25], bound states of two ^{3}He atoms. These Cooper pairs are bosonic and undergo condensation.

The superfluid phase behaves as if it is in a vacuum. This means that the N_0 ^{4}Hein the condensate only have energy when the centre of mass of the superfluid is moving (e.g. when the superfluid is flowing) relative to the lab frame. The condensate flows with zero viscosity, so as long as the flow does not create excitations[26] Another way to give the system energy is if an object moves through the superfluid. There is an energy criteria, known as the Landau criteria, giving the minimum velocity at which the object needs to be moving through the superfluid to generate an excitation.

Include a figure here.

Consider an object of mass M moving through the superfluid. If the object is moving fact enough to generate an excitation, phonon, of energy ε_k and momentum $\hbar k$ then teh conservation laws for energy and momentum state:

$$\frac{1}{2}Mv^2 = \frac{1}{2}Mv_f^2 + \varepsilon_k \tag{6.101}$$

$$Mv = Mv_f + \hbar k, \tag{6.102}$$

where v is the initial velocity of the object and v_f is the object after the phonon mode has been excited. These conservation laws can only be satisfied for a velocity larger than the critical velocity, v_c, corresponding to the lowest energy phonon mode. To find the critical velocity use Equation (6.102) to eliminate v_f from Equation (6.101):

$$M^2 v^2 = M^2 v_f^2 + \hbar^2 k^2, \tag{6.103}$$

$$\Rightarrow \frac{1}{2}Mv_f^2 = \frac{1}{2}Mv^2 + \frac{\hbar^2 k^2}{2M} - v\hbar k, \tag{6.104}$$

$$\Rightarrow \varepsilon_k = \hbar vk - \frac{\hbar^2 k^2}{2M}. \tag{6.105}$$

---

[25]The same phenomena occurs for electrons in a superconductor, electron-phonon interactions cause the electrons to pair up and form a bosonic state whoch can pass through the superconductor without any resistance.

[26]That is the system does not gain enough kinetic energy to excite vibrations, phonons, in the superfluid.

The critical velocity is thus

$$v_c = \text{minimum}\left(\frac{\varepsilon_k + \frac{\hbar^2 k^2}{2M}}{\hbar k}\right),\tag{6.106}$$

which for a very massive object ($M \to \infty$ compared to the $\hbar^2 k^2$) becomes

$$v_c = \text{minimum}\left(\frac{\varepsilon_k}{\hbar k}\right).\tag{6.107}$$

If $v < v_c$ then no excitations are excited. For phonon modes the energy is related to the speed of sound through $\varepsilon_k = \hbar c_{\text{sound}} k$ and $v_c = c_{\text{sound}}$. In ^{4}He the critical velocity is $v_c \simeq 5 \times \text{cms}^{-1}$.

Phonons are not the only excitations possible in superfluid ^{4}He, at higher momenta, values of k, there are quadratic excitations known as rotons. These can be thought of as the quanta of vorticity and are related to vortices that occur in superfluids. While very interesting objects, the study of rotons is unfortunately left for a future course.

7 Transport in Classical Gases

We now turn our attention back to classical gases. In this section we consider the velocity distribution of particles in a gas, and study transport properties in the gas, e.g. diffusion of particles, heat flow.

7.1 Kinetic Theory of an Ideal Gas

Before discussing the Maxwell distribution of velocities we first give a derivation of the ideal gas law by considering a classical gas of molecules in a container.

Include a figure here!

Consider the molecules striking a unit area of the container wall and reflected specularly[27]. The velocity perpendicular to the wall is v_z and the mass of the molecules in M. The change in momentum is thus

$$\Delta p = -2M\,|v_z| = \text{Impulse imparted on the wall.}\tag{7.1}$$

The pressure on the wall is then the impulse imparted from all the molecules striking a unit area in unit time. To understand this a bit better define

$$a(v_z)dv_z$$

to be the number of molecules per unit volume with perpendicular velocity in the range $(v_z, v_z + dv_z)$. Integrating this gives the number density[28],

$$\int a(v_z)dv_z = \frac{N}{V} = n.\tag{7.2}$$

---

[27]That is mirror like reflection where the angle of incidence equals the angle of reflection. Only the z-component of velocity changes, $v_z \to -v_z$.

[28]This is because we are "summing" up the number of particles per unit volume with every possible velocity, giving the total number of particles per unit volume.

To find the number of particles that strike a unit area per unit time we need to modify this. Infinitesimally the volume is $dxdydz$ and the infinitesimal surface area of the container is $dxdy$. Thus we arrive at

$$a(v_z)v_z dv_z,$$

with $v_z = \frac{dz}{dt}$, as the number of particles that strike a unit area per unit time. The momentum change due to these molecules is[29]

$$\Delta p = -2M v_z^2 a(v_z) dv_z. \tag{7.3}$$

This implies that the pressure is

$$P = \int_0^\infty 2M v_z^2 a(v_z) dv_z = M \int_{-\infty}^\infty v_z^2 a(v_z) dv_z, \tag{7.4}$$

where the final integral is the thermal average of v_z^2 times the number density n. Why $v_z^2 n$? This is because $a(v_z) dv_z$ is the number of molecules per unit volume with $v_z \in (v_z, v_z + dv_z)$. The per unit volume in the thermal average is due to this. We thus have that

$$P = M \langle v_z^2 \rangle n. \tag{7.5}$$

We can now invoke the equipartition of energy, that in thermal equilibrium the energy is shared equally between all its forms[30]. For us this just means that the thermal energy is related to the thermal average of the kinetic energy,

$$\frac{1}{2} k_B T = \frac{1}{2} M \langle v_z^2 \rangle. \tag{7.6}$$

Thus

$$P = n k_B T = \frac{N k_B T}{V}, \tag{7.7}$$

the familiar ideal gas law.

As discussed in [KK80] the specular reflection assumption can be relaxed. What is important is that the distribution of velocities is the same before and after reflection.

Now we turn our attention to a derivation of the Maxwell distribution of velocities. Recall that the distribution function for an ideal gas is

$$f(\varepsilon) = \lambda e^{-\beta \varepsilon}, \tag{7.8}$$

the Maxwell-Boltzmann distribution function. Remember that here $f(\varepsilon) = \langle N(\varepsilon) \rangle$ is the probability that the state with energy ε in a cube of volume $V = L^3$ is occupied.

To turn this in to a distribution of velocities proceed as when the density of states was introduced. The average number of particles with state label (read quantum numbers) in the range $(n, n+dn)$ is (Number of states in the range(n,n+dn))$\times$(Probability that a state is occupied).

---

[29] Here we are taking v_z to be the speed in the z-direction which is the modulus of the velocity and thus positive.

[30] More explicitly it states that each degree of freedom has thermal average energy $\frac{1}{2} k_B T$.

For a gas of spin zero particles the number of states in the range is given by the volume of the positive octant of the spherical shell of thickness dn. That is

$$\text{(Number of states in the range(n,n+dn))} = dV_{\text{oct}} = \frac{1}{8}4\pi n^2 dn = \frac{1}{2}\pi n^2 dn. \qquad (7.9)$$

The product of the two factors is thus

$$\text{(Number of states)} \times \text{(occupation probability)} = \frac{1}{2}\pi n^2 dn f(\varepsilon) = \frac{1}{2}\pi n^2 \lambda e^{-\beta\varepsilon} dn. \qquad (7.10)$$

For this to become the probability distribution of velocities we need to relate the state labels to the velocity. This is done by interpreting the energy of a state as the kinetic energy of the particle:

$$\frac{1}{2}Mv^2 = \varepsilon = \frac{\hbar^2}{2M}\left(\frac{\pi n}{L}\right)^2, \qquad (7.11)$$

which implies that

$$n = \frac{ML}{\hbar\pi}v. \qquad (7.12)$$

For a system of N particles in a volume V let the number of particles with speed in the range $(v, v + dv)$ be $NP(v)dv$. This defines the Maxwell distribution function $P(v)$. Putting together everything that we have found so far about the relationship between n and v gives

$$NP(v)dv = dV_{\text{oct}}f(\varepsilon) \qquad (7.13)$$

$$= \frac{1}{2}\pi n^2 \lambda e^{-\beta\varepsilon}\frac{dn}{dv}dv \qquad (7.14)$$

$$= \frac{1}{2}\pi\lambda\left(\frac{ML}{\hbar\pi}\right)^3 v^2 \exp\left(-\frac{\beta Mv^2}{2}\right)dv. \qquad (7.15)$$

Now recall that the fugacity is given by

$$\lambda = \frac{n}{n_q} = \frac{N}{V}\left(\frac{2\pi\hbar^2}{M}\beta\right)^{\frac{3}{2}}, \qquad (7.16)$$

which implies that

$$\frac{1}{2}\pi\lambda\left(\frac{ML}{\hbar\pi}\right)^3 = 4\pi N\left(\frac{M\beta}{2\pi}\right)^{\frac{3}{2}}. \qquad (7.17)$$

Using this relationship we get that

$$P(v) = 4\pi\left(\frac{M\beta}{2\pi}\right)^{\frac{3}{2}} v^2 e^{-\frac{\beta Mv^2}{2}}. \qquad (7.18)$$

This is known as the Maxwell distribution of velocities, and $P(v)dv$ is the probability that a particle has its speed in the range $(v, v + dv)$.

On the problem sheet you will show that the root mean squared velocity is

$$v_{rms} = \sqrt{\langle v^2\rangle} = \left(\frac{3}{M\beta}\right)^{\frac{1}{2}}. \qquad (7.19)$$

For a given temperature T, $P(v)$ shows the probability distribution of particle velocities for the gas. At higher temperatures faster velocities become more likely and the distribution becomes less sharply peaked.

Next we briefly discuss the collision cross section and mean free path for particles in a gas. If we model the particles in a gas a rigid spheres that are moving around there will be collisions between the particles. To estimate the collision rate consider that two particles of diameter d will collide if their centre's pass within distance d of each other.

Each particle sweeps out a path of length L and volume $\pi d^2 L$, d is the radius of the cross sectional circle here as any particle whose centre is within this circle will collide with the particle at the centre. It will collide with any other particle whose centre lies within this volume. The average number of atoms in this volume is $nV = n\pi d^2 L$, the particle concentration multiplied by the volume of the particles trajectory. This is also the average number of collisions.

Another useful quantity is the average distance between collisions, $l = \frac{L}{n\pi d^2 L} = \frac{1}{n\pi d^2}$. This is the average distance a particle moves before a collision occurs also known as the mean free path.

For an ideal gas we can estimate the size of this mean free path l.

For Helium with $d \simeq 2.2\text{Å}$, the diameter of a Helium atom, the collision cross section is $\sigma = \pi d^2 \simeq 15.2 \times 10^{-16}\text{cm}^2$. At $T = 273K$ and atmospheric pressure the concentration of particles in an ideal gas is known as the Loschmidt number,

$$n_0 = \frac{N_A}{V_{\text{Mol}}} = 2.69 \times 10^{19} \text{atoms cm}^{-3}. \tag{7.20}$$

Here N_A is Avagadro's number and V_{Mol} is the molar volume at $T = 273K$. Combining this with the colision cross section leads to the mean free path

$$l = \frac{1}{\pi d^2 n_0} = \frac{1}{\sigma n_0} \simeq 2.44 \times 10^{-5}\text{cm} \sim 1000\, d. \tag{7.21}$$

The associated collision rate is

$$\frac{v_{rms}}{l} \sim \frac{10^5 \text{cms}^{-1}}{10^{-5}\text{cm}} \sim 10^{10}\text{s}^{-1}. \tag{7.22}$$

The concentration depends on the pressure, and thus the mean free path does as well. At a pressure of 10^{-6}atm the concentration reduces by 10^{-6} and the mean free path increases to of the order of 25cm.

This leads to the introduction of the *Knudsen region*. The Knudsen region is when the mean free path is not small compared to the dimensions of the experimental apparatus, e.g. the dimensions of the container containing the gas.

7.2 Transport processes

Consider a system that is **not** in thermal equilibrium, but in a non-equilibrium steady state with a constant flow from one end of the system to the other. e.g. electrons in a conductor or a thermal current if the system is in contact with two reservoirs at different temperatures.

If $T_1 > T_2$ energy will flow through the system from reservoir 1 to reservoir 2. This energy flow increases the total entropy, the entropy of reservoir 1 plus entropy of reservoir 2 plus entropy of the system. The temperature gradient is the driving force for the energy transfer.

There is a linear regime where Flux $\propto$ force,

$$\text{Flux} = (\text{coefficient}) \times (\text{driving force}), \tag{7.23}$$

provided that the force is not too large. Laws like this are called linear phenomenological laws, e.g. Ohm's law for conduction. See Table. 6 for examples of phenomenological transport laws and the gradients that drive them.

The definition of the flux density of a quantity A is

$$J_A = \text{net quantity of } A \text{ transported across unit area in unit time.} \tag{7.24}$$

The net transport is the transport in one direction minus the transport in the other direction, e.g. transport $R_1 \to R_2$ minus transport $R_2 - R_1$.

Effect	Flux of particle property	Gradient	Law	Approximate Coefficient
Diffusion (Fick's Law)	Number	$\frac{dn}{dz}$	$J_n = -D\nabla n$	$D = \frac{1}{3}\bar{c}l$
Viscosity (Newtonian Viscosity)	Transverse Momentum	$M\frac{dv_x}{dz}$	$J_z^x = -\eta\frac{dv_x}{dz}$	$\eta = \frac{1}{3}\rho\bar{c}l$
Thermal Conductivity (Fourier's Law)	Energy	$\tilde{C}_V\frac{d\beta^{-1}}{dz}$	$J_u = -K\nabla\beta^{-1}$	$K = \frac{1}{3}\tilde{C}_V\bar{c}l$
Electrical Conductivity (Ohm's Law)	Charge	$E_z = -\frac{d\varphi}{dz}$	$J_q = \sigma E$	$\sigma = \frac{nq^2l}{M\bar{c}}$

Table 6: A variety of transport laws and the associated gradients that drive the transport processes.

Example 7.1. Particle Diffusion:
Consider the diffusive case where the reservoirs are at the same temperature, $T_1 = T_2$, but different chemical potentials, $\mu_1 \neq \mu_2$. Since the difference in chemical potential is caused by a difference in particle concentration, this means that there will be a flow of particles through the system to bring the chemical potentials towards equilibrium. The driving force is thus isothermal diffusion and the flow of particles in governed by Fick's law

$$\vec{J}_n = -D\nabla n, \tag{7.25}$$

with D the diffusivity, n the concentration, and $\vec{J}_n$ the flux density of particles.

Particles travel freely over distances up to the order of the mean free path before colliding. Assume that in a collision at position z the particles reach a local equilibrium with $\mu(z), n(z)$. Let $l_z = l\cos\theta$ be the projection of the mean free path onto the z-axis. Across the xy-plane at

z there is a particle flux in the positive z-direction $\frac{1}{2}n(z - l_z)\bar{c}_z$, with $\bar{c}_z = \langle |v| \rangle \cos\theta$ the average speed in the z-direction and $n(z - l_z)$ the particle concentration at position $z - l_z$. The flux in the negative z-direction is $-\frac{1}{2}n(z + l_z)\bar{c}_z$. The net flux has contributions not just from the z-axis, but from all the forward directions through a hemisphere. As such it is the average of

$$J_n^z = \frac{1}{2}\left(n(z - l_z) - n(z + l_z)\right)\bar{c}_z = -\frac{dn}{dz}\bar{c}_z l_z, \tag{7.26}$$

over all directions through the hemisphere. To find this we need the average values of $\bar{c}_z l_z = \bar{c}l\cos^2\theta$. The average is

$$\begin{aligned}\langle \bar{c}_z l_z \rangle &= \bar{c}l\frac{\int_0^{2\pi}\int_0^{\frac{\pi}{2}}\cos^2\theta\sin\theta d\theta d\varphi}{2\pi} \\ &= \frac{1}{3}\bar{c}l.\end{aligned} \tag{7.27}$$

Thus

$$\langle J_n^z \rangle = -\frac{1}{3}\bar{c}l\frac{dn}{dz}. \tag{7.28}$$

This is the prototypical example of a transport problem.

In particle diffusion we are studying the transport of particles. The other transport processes involve the transport of a property by particles:

- Thermal conductivity, transport of energy by particles.

- Viscosity, transport of momentum by particles.

- Electrical conductivity, transport of charge by particles.

The linear transport coefficient is thus proportional to the diffusivity D.

To get a feel for the general picture let $\rho_A =$ concentration of quantity A. If A is a quantity like charge or mass that is the same for all particles, then the flux in the z-direction is

$$J_A^z = \rho_A \langle v_z \rangle. \tag{7.29}$$

Here $\langle v_z \rangle$ is the mean drift velocity, this is zero in thermal equilibrium.

If A is a quantity which depends on the particle velocity, such as energy or momentum, then

$$J_A^z = f_A \rho_A \langle v_z \rangle, \tag{7.30}$$

where f_A is a quantity with $|f_A|$ of order unity, it depends on the velocity dependence of A through the Boltzmann transport equation. We may see more about this later. For simplicity here take $f_A = 1$. The phenomenological transport law is then

$$\vec{J}_A = -D\nabla\rho_A. \tag{7.31}$$

Example 7.2. Thermal Conductivity: For thermal conductivity Fourier's law states,

$$\vec{J}_u = -K\nabla\beta^{-1} = -Kk_B\nabla T, \tag{7.32}$$

with $\vec{J}_u$ the energy flux density, K the thermal conductivity, and ∇T the temperature gradient. This form of Fourier's law assumes energy flow but not particle flow. If particle flow is included this leads to

$$J_u^z \simeq \rho_u\langle v_z\rangle. \tag{7.33}$$

The above expression is valid to within a term of order unity, the f_u from above. By analogy with the diffusion case the right hand side is equivalent to

$$-D\frac{d\rho_u}{dx} = -D\frac{\partial\rho_u}{\partial\beta^{-1}}\frac{d\beta^{-1}}{dx}, \tag{7.34}$$

which describes the diffusion of energy. Note that

$$\frac{\partial\rho_u}{\partial\beta^{-1}} = \tilde{C}_V \tag{7.35}$$

is the heat capacity per unit volume. This implies that

$$\vec{J}_u = -D\tilde{C}_V\nabla\beta^{-1}, \tag{7.36}$$

and $K = D\tilde{C}_V = \frac{1}{3}\tilde{C}_V\bar{c}l$. In particular we find that the thermal conductivity of a gas does not explicitly depend on the pressure. This is true until the pressure is very low and we enter the Knudsen region.

Example 7.3. *Viscosity: Next consider viscosity. This is a measure of the diffusion of momentum parallel to the flow velocity, and transverse to the gradient of the flow velocity. e.g. if the flow is in the x direction and the flow velocity gradient is in the z-direction then the shear stress is given by

$$X_z = -\eta\frac{dv_x}{dz} = J_z(p_x). \tag{7.37}$$

Here X_z is the x-component of the shear force exerted by the gas on a unit area of the xy plane normal to the z-axis. Newton's second law implies that X_z acts if there is a net momentum flux density. Recall from the diffusion case that $J_n^z = n\langle v_z\rangle = -D\frac{dn}{dz}$.

The transverse momentum density is nMv_x, giving the z-flux denisty as

$$nMv_x\langle v_z\rangle = -D\frac{d}{dz}\left(nMv_x\right) = -\eta\frac{dv_x}{dz}, \tag{7.38}$$

again this is true up to a velocity dependent function of order unity. Let $\rho = nM$ be the mass density, then

$$J_x(p_x) = \rho\langle v_z\rangle v_x = -D\rho\frac{dv_x}{dz} = -\eta\frac{dv_x}{dz}. \tag{7.39}$$

Using that $D = \frac{1}{3}\bar{c}l$ gives that

$$\eta = \frac{1}{3}\bar{c}l\rho. \tag{7.40}$$

As with the thermal conductivity, the viscosity looks to be independent of the pressure. However, this fails at very high pressure when the particles are nearly always in contact. It also fails at very low pressure when the gas enters the Knudsen region.

The viscosity is usually easier to measure than the diffusivity. Thus it is useful to note that

$$D = \frac{\eta}{\rho}, \qquad K = \frac{\eta \tilde{C}_V}{\rho}. \tag{7.41}$$

7.3 Generalised Forces

Any transport process leads to entropy transfer between the parts of the system. The rate of change of entropy is related to the flux density of particles and energy. At constant volume we know that

$$d\sigma = \beta dU - \mu \beta dN, \tag{7.42}$$

where $\sigma = \frac{S}{k_B}$ is the fundamental entropy. By analogy the entropy current is

$$\vec{J}_\sigma = \beta \vec{J}_u - \mu \beta \vec{J}_n. \tag{7.43}$$

Let $\tilde{\sigma}$ be the fundamental entropy density, and $\frac{\partial \tilde{\sigma}}{\partial t}$ its net rate of change at a fixed position $\vec{r}$. Then there is a continuity equation, at unit volume,

$$\frac{\partial \tilde{\sigma}}{\partial t} = g_\sigma - \nabla \cdot \vec{J}_\sigma. \tag{7.44}$$

Here g_σ is the rate of production of entropy and $\nabla \cdot \vec{J}_\sigma$ is the loss of entropy due to the transport current.

The energy and total particle number are conserved in a transfer process so their continuity equations are

$$\frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_u, \tag{7.45}$$

$$\frac{\partial n}{\partial t} = -\nabla \cdot \vec{J}_n. \tag{7.46}$$

Expanding the entropy current gives

$$\nabla \cdot \vec{J}_\sigma = \beta \nabla \cdot \vec{J}_u + \vec{J}_u \cdot \nabla \beta - \mu \beta \nabla \cdot \vec{J}_n - \vec{J}_n \cdot \nabla (\mu \beta), \tag{7.47}$$

while we also have that

$$\frac{\partial \tilde{\sigma}}{\partial t} = \beta \frac{\partial u}{\partial t} - \mu \beta \frac{\partial n}{\partial t}. \tag{7.48}$$

Putting it all together gives that

$$g_\sigma = \vec{J}_u \cdot \nabla \beta + \vec{J}_n \cdot \nabla (-\mu \beta) = \vec{J}_u \cdot \vec{F}_u + \vec{J}_n \cdot \vec{F}_n, \tag{7.49}$$

where $\vec{F}_u$ and $\vec{F}_n$ are generalised forces defined by the above equation. They are forces in the sense that they are the gradient of an energy.

65

Example 7.4. Einstein Relation: The generalised forces picture leads us to the Einstein relations. Consider an isothermal process,

$$\vec{F}_u = 0, \qquad \vec{F}_n = -\beta \nabla \mu = -\beta \left(\nabla \mu_{\text{int}} + \nabla \mu_{\text{ext}} \right), \tag{7.50}$$

where μ_{int} and μ_{ext} are the internal and external chemical potentials respectively. For an ideal gas we know that

$$\mu_{\text{int}} = \beta^{-1} \ln \left(\frac{n}{n_Q} \right) \qquad \Rightarrow \nabla \mu_{\text{int}} = (\beta n)^{-1} \nabla n. \tag{7.51}$$

For an electrostatic potential we also know that

$$\mu_{\text{ext}} = q \nabla \varphi = -q \vec{E}, \tag{7.52}$$

so that

$$\vec{F}_n = -n^{-1} \nabla n + \beta^{-1} q \vec{E} = -\beta \left(\beta^{-1} n^{-1} \nabla n - q \vec{E} \right). \tag{7.53}$$

The particle flux density also has two terms

$$\vec{J}_n = -D \nabla n + n \tilde{\mu} \vec{E}, \tag{7.54}$$

where D is the diffusivity and $\tilde{\mu}$ is the mobility, the ratio of coefficients is $\frac{D}{n\tilde{\mu}}$. For the generalised force the ratio of coefficients is $\frac{1}{q\beta n}$. By dimensional analysis these ratios must be the same, this is because ∇n and $\vec{E}$ contribute in the same proportions to both terms, thus

$$D = \frac{\tilde{\mu}}{q\beta}. \tag{7.55}$$

This is known as the Einstein relation between diffusivity and mobility. There are many such relations and other ways to derive them.

7.4   Boltzmann Transport Equation

The basis of the classical theory of transport processes is the Boltzmann transport equation. This is a partial differential equation in six variables, 3 positions and 3 velocities, describing the evolution of a distribution function. We will consider the examples of the classical Maxwell-Boltzmann and the Fermi-Dirac distribution.

Consider a classical distribution function $f(\vec{r}, \vec{v})$,

$$f(\vec{r}, \vec{v}) d\vec{r} d\vec{v} = \text{number of particles in } d\vec{r} d\vec{v}, \tag{7.56}$$

where we interpret $d\vec{r} d\vec{v}$ as the volume element of the six dimensional space. The Boltzmann equation is derived by considering an infinitesimal time displacement of the distribution $f(\vec{r}, \vec{v})$. Liouville's theorem[31] states that the distribution function is unchanged by this time displacement,

$$f(t + dt, \vec{r} + d\vec{r}, \vec{v} + d\vec{v}) = f(t, \vec{r}, \vec{v}). \tag{7.57}$$

---

[31]An important result in classical mechanics which says that "the phase-space distribution function is constant along the trajectories of the system". In more mathematical terms, the action of a symplectomorphism does not change the volume of a region of phase space.

This is true in the absence of collisions. With collisions, there will be a change,

$$f(t + dt, \vec{r} + d\vec{r}, \vec{v} + d\vec{v}) - f(t, \vec{r}, \vec{v}) = dt \left(\frac{\partial f}{\partial t} \right)_{\text{collisions}}. \tag{7.58}$$

Using the chain rule this becomes

$$\left(\frac{\partial f}{\partial t} \right) dt + d\vec{r} \cdot \nabla_{\vec{r}} f + d\vec{v} \cdot \nabla_{\vec{v}} f = dt \left(\frac{\partial f}{\partial t} \right)_{\text{collisions}}, \tag{7.59}$$

with $\nabla_{\vec{r}} f$ the gradient of f with respect to the spatial coordinates x, y, z, and $\nabla_{\vec{v}} f$ the gradient of f with respect to the velocity coordinates v_x, v_y, v_z. Calling the acceleration $\vec{\alpha} = \frac{d\vec{v}}{dt}$ this becomes

$$\left(\frac{\partial f}{\partial t} \right) + \vec{v} \cdot \nabla_{\vec{r}} f + \vec{\alpha} \cdot \nabla_{\vec{c}} f = \left(\frac{\partial f}{\partial t} \right)_{\text{collisions}} \tag{7.60}$$

which is the Boltzmann transport equation.

It is often convenient to introduce a relaxation time, τ_c, through

$$\left(\frac{\partial f}{\partial t} \right)_{\text{collisions}} = -\frac{f - f_0}{\tau_c}, \tag{7.61}$$

where f_0 is the distribution at thermal equilibrium. Assume that a non-equilibrium velocity distribution is reached through the action of external forces. If the forces are suddenly removed then the distribution decays to equilibrium over a time scale governed by τ_c. In other words the distribution *relaxes* to equilibrium through scattering events. To see this explicitly consider

$$-\frac{f - f_0}{\tau_c} = \left(\frac{\partial f}{\partial t} \right)_{\text{collisions}} = \left(\frac{\partial f - f_0}{\partial t} \right)_{\text{collisions}}, \qquad \text{as} \quad \frac{\partial f_0}{\partial t}. \tag{7.62}$$

This is solved by

$$(f - f_0)_t = (f - f_0)_{t=0} \, e^{-\frac{t}{\tau_c}}. \tag{7.63}$$

Thus τ_c is the time it takes for $f - f_0$ to decrease by e^{-1}. In the relaxation time approximation the Boltzmann equation is

$$\left(\frac{\partial f}{\partial t} \right) + \vec{v} \cdot \nabla_{\vec{r}} f + \vec{\alpha} \cdot \nabla_{\vec{c}} f = -\frac{f - f_0}{\tau_c}. \tag{7.64}$$

A steady state is defined as a configuration with

$$\left(\frac{\partial f}{\partial t} \right) = 0. \tag{7.65}$$

We can now demonstrate how the Boltzmann transport equation leads to the phenomenological transport laws that we encountered earlier.

Example 7.5. Particle Diffusion.
Consider an isothermal system with a concentration gradient. For a non-equilibrium distribution f only varying in the x-direction[32] the relaxation time approximation of the Boltzmann equation is

$$v_x \frac{\partial f}{\partial x} = -\frac{f - f_0}{\tau_c}. \tag{7.66}$$

---

[32]That is f does not depend on y, z or any of the velocities.

This equation is solved iteratively by writing f in terms of the equilibrium distribution. To first order the distribution is

$$f_1 \simeq f_0 - v_x \tau_c \frac{\partial f_0}{\partial x}. \tag{7.67}$$

Now iterate this expression,

$$f_2 \simeq f_0 - v_x \tau_c \frac{\partial f_1}{\partial x} = f_0 - v_x \tau_c \frac{\partial f_0}{\partial x} + v_x^2 \tau_c^2 \frac{\partial^2 f_0}{\partial x^2}, \tag{7.68}$$

where we have assumed that v_x and τ_c are constant in x. This iterative approach is needed to account for non-linear effects. We will not need to use this in our example. The explicit details depend on the particular distribution f.

Classical Distribution. Take the equilibrium distribution to be

$$f_0 = f_{\mathrm{MB}} = e^{(\mu - \varepsilon)\beta}, \tag{7.69}$$

the classical Maxwell-Boltzmann distribution. The transport equation is linear in f and f_0 so we can normalise the distribution however we want, e.g. this is why we can take $f_0 = e^{(\mu - \varepsilon)\beta}$ rather than $f\,dvdt = \#$ particles in $dvdt$. For the Maxwell-Boltzmann distribution we have that

$$\frac{df_0}{dx} = \frac{df_0}{d\mu}\frac{d\mu}{dx} = \beta f_0 \frac{d\mu}{dx}, \tag{7.70}$$

so the first order solution is

$$f_1 = f_0 - v_x \tau_c \beta f_0 \frac{d\mu}{dx}. \tag{7.71}$$

The particle flux density is related to the distribution function and the density of states[33] per unit volume,

$$\tilde{\mathcal{D}}(\varepsilon) = \frac{1}{4\pi}\left(\frac{2M}{\hbar^2}\right)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}, \tag{7.72}$$

by integration

$$J_n^x = \int v_x f \tilde{\mathcal{D}}(\varepsilon)d\varepsilon. \tag{7.73}$$

For the first order solution this becomes

$$J_n^x = \int v_x f_0 \tilde{\mathcal{D}}(\varepsilon)d\varepsilon - \frac{d\mu}{dx}\int v_x^2 \tau_c f_0 \beta \tilde{\mathcal{D}}(\varepsilon)d\varepsilon. \tag{7.74}$$

The first term vanishes because the net particle flux vanishes for the equilibrium distribution[34]. The second integral does not vanish. To evaluate it we need to understand the velocity dependence of the relaxation time.

If τ_c is a constant then,

$$J_n^x = -\frac{d\mu}{dx}\tau_c \beta \int v_x^2 f_0 \tilde{\mathcal{D}}(\varepsilon)d\varepsilon. \tag{7.75}$$

---

[33]This is the density of states for a spin zero particle!

[34]To see this explicitly we want to express everything in terms of the velocity through the identification $\varepsilon = \frac{1}{2}mv^2$, and the approximation that $v_x^2 = \frac{1}{3}v^2$. Then $d\varepsilon = mvdv$ and the integrand is an odd function of v which vanishes when integrated over all velocities.

This is evaluated by making the assumption that the velocity is equally shared between the three directions, at least on average i.e under the integral, so that

$$\int v_x^2 f_0 \tilde{\mathcal{D}}(\varepsilon) d\varepsilon = \frac{1}{3} \int v^2 f_0 \tilde{\mathcal{D}}(\varepsilon) d\varepsilon = \frac{2}{3m} \int \left(\frac{1}{2} m v^2 \right) f_0 \tilde{\mathcal{D}}(\varepsilon) d\varepsilon = \frac{2}{3m} \frac{3}{2} \frac{n}{\beta} = \frac{n}{m\beta}. \quad (7.76)$$

The integral is the kinetic energy density, $\frac{3}{2} \frac{n}{\beta}$ of the particles, this is related to the equipartition of the energy. Also note that the concentration is given by

$$n = \int f_0 \tilde{\mathcal{D}}(\varepsilon) d\varepsilon. \quad (7.77)$$

We are thus left with the diffusion equation

$$j_n^x = -\frac{n\tau_c}{m} \frac{d\mu}{dx} = -\frac{\tau_c}{\beta m} \frac{dn}{dx}, \quad (7.78)$$

where we have used the ideal gas relation $\mu = \beta^{-1} \ln \frac{n}{n_Q}$. The Diffusivity is given by

$$D = \frac{\tau_c}{\beta m} = \frac{1}{3} \langle v^2 \rangle \tau_c, \quad (7.79)$$

where we have used that the thermal average of the velocity is given by $\langle v^2 \rangle = \frac{3}{\beta}$ which follows from the same equipartition of energy argument as is used above.

Next consider the case $\tau_c = \frac{l}{v}$, where l is the mean free path. Now the particle flux density is

$$J_n^x = -\frac{d\mu}{dx} l\beta \int \frac{v_x^2}{v} f_0 \tilde{\mathcal{D}}(\varepsilon) d\varepsilon = -\frac{1}{3} \frac{d\mu}{dx} l\beta \int v f_0 \tilde{\mathcal{D}}(\varepsilon) d\varepsilon. \quad (7.80)$$

The integral is just the thermal average speed times the concentration $n\langle v \rangle = n\bar{c}$, giving

$$J_n^x = -\frac{1}{3} l\bar{c} n \beta \frac{d\mu}{dx} = -\frac{1}{3} l\bar{c} \frac{dn}{dx}, \quad (7.81)$$

this is just Fick's law with the same diffusivity as we found previously $D = \frac{1}{3} l\bar{c}$.

Fermi-Dirac Distribution. Now we tackle the case of the equilibrium distribution being the Fermi-Dirac distribution

$$f_0 = f_{FD} = \frac{1}{e^{(\varepsilon - \mu)\beta} + 1}. \quad (7.82)$$

For the Boltzmann equation we need the derivative of the distribution with respect to the chemical potential, $\frac{df_0}{d\mu}$. Previously we reasoned that this is a delta function for temperatures far below the Fermi temperature, equivalently energies such that $\mu \ll \beta^{-1}$.

Another justification of this is as follows: consider the integral

$$\int_0^\infty F(\varepsilon) \frac{df_0}{d\mu} d\varepsilon, \quad (7.83)$$

with F an arbitrary function of the energy. At low temperatures this is very large for $\varepsilon \simeq \mu$ so if $F(\varepsilon)$ is not wildly varying near μ we can replace it by $F(\mu)$,

$$\int_0^\infty F(\varepsilon) \frac{df_0}{d\mu} d\varepsilon, = F(\mu) \int_0^\infty \frac{df_0}{d\mu} d\varepsilon \tag{7.84}$$

$$= -F(\mu) \int_0^\infty \frac{df_0}{d\varepsilon} d\varepsilon \tag{7.85}$$

$$= -F(\mu) \left[f_0(\infty) - f_0(0) \right] \tag{7.86}$$

$$= F(\mu) f_0(0), \tag{7.87}$$

since $f_0(\infty) = 0$. At low temperatures, $\mu\beta \ll 1$, $f_0(0) \simeq 1$ so

$$\int_0^\infty F(\varepsilon) \frac{df_0}{d\mu} d\varepsilon \simeq F(\mu), \tag{7.88}$$

which implies that

$$\frac{df_0}{d\mu} = \delta(\varepsilon - \mu). \tag{7.89}$$

Thus

$$\frac{df_0}{dx} = \delta(\varepsilon - \mu) \frac{d\mu}{dx}. \tag{7.90}$$

The particle flux density thus becomes[35]

$$J_n^x = -\frac{d\mu}{dx} \tau_c \int v_x \delta(\varepsilon - \mu) \tilde{\mathcal{D}}(\varepsilon) d\varepsilon, \tag{7.91}$$

with τ_c the relaxation time at $\varepsilon = \mu$. This integral can be evaluated in the same way as above,

$$\int v_x \delta(\varepsilon - \mu) \tilde{\mathcal{D}}(\varepsilon) d\varepsilon = \frac{1}{3} \int v \delta(\varepsilon - \mu) \tilde{\mathcal{D}}(\varepsilon) d\varepsilon = \frac{1}{3} v_F^2 \frac{3n}{2\varepsilon_{F0}} = \frac{n}{m}. \tag{7.92}$$

Here we have used that for $T \ll T_F$ the density of states per unit volume is $\tilde{\mathcal{D}}(\mu) = \frac{3n}{\varepsilon_{F0}}$ and $2\varepsilon_{F0} = mv_F^2$. Thus

$$J_n^x = -\frac{d\mu}{dx} \tau_c \frac{n}{m}. \tag{7.93}$$

For $T \ll T_F$ we can evaluate the derivative of the chemical potential using

$$\mu = \frac{\hbar^2}{2m} \left(3\pi^2 n \right)^{\frac{2}{3}}, \tag{7.94}$$

$$\Rightarrow \frac{d\mu}{dx} = \frac{2}{3} \frac{\hbar^2}{2m} \left(3\pi^2 \right)^{\frac{2}{3}} n^{-\frac{1}{3}} \frac{dn}{dx} \tag{7.95}$$

$$= \frac{3}{2} \frac{\varepsilon_{F0}}{n} \frac{dn}{dx}. \tag{7.96}$$

This gives

$$J_n^x = -\frac{2\tau_c}{3n} \varepsilon_{F0} \frac{n}{m} \frac{dn}{dx} = -\frac{1}{3} \tau_c v_F^2 \frac{dn}{dx}, \tag{7.97}$$

A diffusion equation with diffusivity

$$D = \frac{1}{3} v_F^2 \tau_c \tag{7.98}$$

Finding this diffusion equation was no more complicated in the Fermi-Dirac case than for a classical gas.

---

[35] we have again used the first order expansion for f and used that the first integral term vanishes.

Electrical Conductivity. The isothermal electrical conductivity follows from the same argument if the particle flux density is multiplied by the charge q, and $\frac{d\mu}{dx}$ is replaced by $q\frac{d\varphi}{dx} = -qE_x$, the gradient of the electrostatic potential.

This implies that the current density is

$$\vec{J}_q = \frac{nq^2\tau_c}{m}\vec{E} = \sigma\vec{E}, \tag{7.99}$$

with σ the conductivity, for both the classical gas and the Fermi-Dirac distribution.

8 Heat Conduction Equation

The form of the Phenomenological transport laws that we encountered above are closely related to some equations that you may have met in a Fourier analysis course. As the total particle number is conserved[36] there is a continuity equation

$$\frac{\partial n}{\partial t} + \nabla \cdot \vec{J}_n = 0. \tag{8.1}$$

Now consider Fick's law, Equation (7.25), and take its divergence, noting that $\nabla \cdot \nabla n = \Delta n$, to find

$$\frac{\partial n}{\partial t} = D\Delta n. \tag{8.2}$$

This is known as the diffusion equation, and it has a variety of interesting solutions found by considering the Fourier transform[37].

If we apply the same argument to Fourier's law $\vec{J}_u = -K\nabla\beta^{-1}$, and use the continuity equation for energy density,

$$\frac{\partial \rho_u}{\partial t} + \nabla \cdot \vec{J}_u = \tilde{C}_V \frac{\partial \beta^{-1}}{\partial t} + \nabla \cdot \vec{J}_u = 0, \tag{8.3}$$

we arrive at the heat equation

$$\frac{\partial T}{\partial t} = D_T\Delta T, \tag{8.4}$$

where $D_T = \frac{K}{\tilde{C}_V}$ is the Thermal diffusivity. The heat equation is another example of a type of partial differential equation known generally as a diffusion equation. This is because useful solutions are pulses that spread out, diffuse, with time.

One trick to solve an equation of the form

$$\frac{\partial \Theta}{\partial t} = D\nabla\Theta, \tag{8.5}$$

is to take a plane wave Ansatz,

$$\Theta = \Theta_0 e^{i(\vec{k}\cdot\vec{r} - \omega t)}, \tag{8.6}$$

---

[36]We are not allowing the creation of new particles, just their movement between parts of the total system.

[37]Here we will just quote the solutions and you can check them by substituting in rather than Fourier transforming

with wave vector $\vec{k}$ and angular frequency ω. These solutions are highly damped waves since $\vec{k}^2$ is complex. Substitution into Equation (8.5) leads to

$$\vec{k}^2 = i\frac{\omega}{D}, \tag{8.7}$$

which is known as a dispersion relation. In fact any equation which give the frequency as a function of the wave vector is known as a dispersion relation e.g. $\omega = kc_{\text{sound}}$ for phonons.

A nice example of using the damped wave solution is the following.

Example 8.1. Penetration of Temperature Oscillations
Consider the variation of temperature in a $1D$ semi infinite medium, e.g. $z \in [0, \infty)$ with boundary condition

$$\Theta(0, t) = \Theta_0 \cos \omega t = \Theta_0 \Re \left\{ e^{i(\vec{k}\cdot\vec{r} - \omega t)} \right\}, \tag{8.8}$$

with Θ_0 real.

Then for $z > 0$ the solution is

$$\Theta(z, t) = \Theta_0 \Re \left\{ e^{i(\vec{k}\cdot\vec{r} - \omega t)} \right\} \tag{8.9}$$

$$= \Theta_0 \Re \left\{ \exp\left(i^{\frac{3}{2}} \sqrt{\frac{\omega}{D}} z - i\omega t \right) \right\} \quad \text{using } k = \sqrt{i\frac{\omega}{D}}, \tag{8.10}$$

$$= \Theta_0 e^{-\sqrt{\frac{\omega}{2D}}} \Re \left\{ \exp\left(i \left[\sqrt{\frac{\omega}{2D}} z - \omega t \right] \right) \right\} \quad \text{using } i^{\frac{3}{2}} = \frac{i-1}{\sqrt{2}}, \tag{8.11}$$

$$= \Theta_0 e^{-\frac{z}{\delta}} \Re \left\{ \exp\left(i \left[\frac{z}{\delta} - \omega t \right] \right) \right\} \quad \text{where } \delta = \sqrt{\frac{2D}{\omega}}, \tag{8.12}$$

$$= \Theta_0 e^{-\frac{z}{\delta}} \cos\left(\frac{z}{\delta} - \omega t \right). \tag{8.13}$$

The parameter δ introduced above has units of length and is called the characteristic penetration depth of the temperature variation. e.g. at $z = \delta$ the amplitude of the oscillation is reduced by e^{-1}. Often δ is called the skin depth, such as the depth of magnetic field penetration in a superconductor. If we estimate the thermal diffusivity of soil to be $D \simeq 1 \times 10^{-3} \text{cm}^3\text{s}^{-1}$ then we can estimate δ for both the day-night heating-cooling cycle and the annual summer-winter temperature variation. You will consider this in more detail on problem sheet 5. The angular frequency of each cycle is different; for day-night variation

$$\omega = \frac{2\pi}{1 \text{ day}} = 0.73 \times 10^{-4} \text{s}^{-1} \qquad \Rightarrow \delta \simeq 5\text{cm}, \tag{8.14}$$

for the annual cycle find

$$\delta \simeq 1m. \tag{8.15}$$

Thus at a depth of 10cm the day night cycle of temperature variation averages out and the temperature is approximately constant. However, to cancel out the annual variation requires going to a greater depth. In reality, D is highly sensitive to soil composition.

Development of a pulse. Next we consider pulsed solutions to Equation (8.5):

$$\Theta\left(x,t\right) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}. \tag{8.16}$$

This is a normalised Gaussian function, you will work with the $2D$ and $3D$ solutions on problem sheet 5. To find this solution take the Fourier transform of Equation (8.5), then solve the equation then take the inverse Fourier transform.

The solution in Equation (8.16) is a pulse that spreads out with time. Initially the pulse is a delta function,

$$\Theta(x,0) = \delta(x) = \begin{cases} \infty & \text{when } x = 0 \\ 0 & \text{else} \end{cases}, \tag{8.17}$$

with

$$\int_{-\infty}^{\infty} \delta(x)dx = 1. \tag{8.18}$$

This can be any sort of pulse; temperature, concentration, etc. For example if we have a brief laser pulse depositing heat Q on a surface; we get a heat pulse spreading out from the impact point,

$$\Theta(x,t) = \frac{2Q}{\tilde{C}_V} \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}. \tag{8.19}$$

The factor of 2 appears here because all the heat is flowing away from the impact point, where as the flow above was symmetric.

A pulse like this spreads out with increasing t with mean squared,

$$\langle x^2 \rangle = \frac{\int x^2 \Theta(x,t)dx}{\int \Theta(x,t)dx} = 2Dt, \tag{8.20}$$

demonstrating this requires evaluating two Gaussian integrals. The rms position is thus

$$x_{\text{rms}} = \sqrt{\langle x^2 \rangle} = \sqrt{2Dt}. \tag{8.21}$$

There is a relation to Brownian motion here which we may see more about later. Think of the pulse as a temperature distribution, its width is proportional to $t^{\frac{1}{2}}$. This is a general characteristic of diffusion in $1D$ and of random walks in $1D$. It differs from the plane wave pulse which has dispersion $\omega = vk$. Consider a random walk with step size t_0, after N steps the time is $t = Nt_0$ and the rms position is

$$x_{\text{rms}}(t) = \sqrt{2Dt_0}N^{\frac{1}{2}}. \tag{8.22}$$

This is observed in Brownian motion where the rms position is proportional to the square root of the number of steps.

Diffusion with a boundary. Let us return to a situation where we have diffusion on a semi-infinite interval, $x \in [0, \infty)$, with a boundary at $x = 0$. Given a solution to Equation (8.5) we can ask if integrating or differentiating it leads to another solution. In some cases it does. For example, consider:

$$\Theta(x, t) = \frac{1}{\sqrt{4\pi Dt}} \int_0^x e^{-\frac{v^2}{4Dt}} dv, \tag{8.23}$$

$$= \frac{1}{\pi} \int_0^u e^{-s^2} ds, \quad \text{where } s = \frac{v}{\sqrt{4Dt}} \text{ and } u = \frac{x}{\sqrt{4Dt}}, \tag{8.24}$$

$$= \operatorname{erf}(u). \tag{8.25}$$

Here $\operatorname{erf}(u)$ is the error function. It satisfies

$$\operatorname{erf}(0) = 0, \qquad \lim_{x \to \infty} \operatorname{erf}(x) = 1, \tag{8.26}$$

and its values can be looked up in a table.

If we consider a situation of a temperature pulse in a medium with a fixed boundary, and boundary conditions

$$\Theta(0) = \Theta_0, \qquad \Theta(\infty) = 0, \tag{8.27}$$

then the solution is

$$\Theta(x, t) = \Theta_0 \left[1 - \operatorname{erf}\left(\frac{x}{\sqrt{4Dt}} \right) \right]. \tag{8.28}$$

Note that the distance at which $\Theta(x, t)$ reaches a specific value is proportional to $\sqrt{4Dt}$. This approach is useful when studying the diffusion of impurities in a semiconductor.

Time-independent Distribution. Consider a time independent function $\Theta(x)$, applied to this function the diffusion equation reduces to the Laplace equation,

$$\Delta \Theta(x\vec{x}) = 0. \tag{8.29}$$

Focus on the case $(x, y, z) \in \mathbb{R}^2 \times [0, \infty)$ with

$$\Theta(x, y, 0) = \Theta_0 \sin kx, \tag{8.30}$$

on the boundary. In the medium the solution becomes

$$\Theta(x, y, z) = \Theta \sin kx e^{-kz}, \tag{8.31}$$

e.g. the temperature variation is damped exponentially with distance from the boundary. This temperature distribution must be maintained by a constant source of heat at $z = 0$. It can be used to model situations where a specific point is being constantly heated, or where an electrode is constantly injecting a current into a metal.

A   More on Differentials

In lecture 1 we encountered the concept of an exact differential, and implicitly encountered the concept of an inexact differential. I want to give a bit more information and some examples. If you have any questions about this feel free to email me.

A.1 Exact differentials

The definition of an exact differential given in the lecture notes is the following:

Definition A.1. *A function $F(x_1, x_2)$ of at least two independent variables, x_1, x_2 has differential*

$$dF = \left(\frac{\partial F}{\partial x_1}\right)_{x_2} dx_1 + \left(\frac{\partial F}{\partial x_2}\right)_{x_1} dx_2, \tag{A.1}$$

where $\left(\frac{\partial F}{\partial x_1}\right)_{x_2}$ means the derivative of F with respect to x_1 holding x_2 constant. If F and its derivative are continuous and

$$\left(\frac{\partial}{\partial x_1}\left(\frac{\partial F}{\partial x_2}\right)_{x_1}\right)_{x_2} = \left(\frac{\partial}{\partial x_2}\left(\frac{\partial F}{\partial x_1}\right)_{x_2}\right)_{x_1} \tag{A.2}$$

e.g. the partial derivatives commute, then dF is called an exact differential.

This condition of commuting partial derivatives is true for most sensible examples of functions. A function that does not satisfy this is

$$f(x, y) = \begin{cases} \dfrac{xy\left(x^2 - y^2\right)}{x^2 + y^2}, & (x, y) \neq (0, 0) \\ 0 & (x, y) = (0, 0). \end{cases} \tag{A.3}$$

This function is continuous and its partial derivatives are continuous. However, the second partial derivatives, $\frac{\partial^2 f}{\partial x \partial y}$ etc, are not continuous. This example is taken from the wikipedia page Symmetry of second derivatives[38]. As long as we avoid pathological examples, if we write down a function $F(x_1, x_2)$ then it will have an exact differential.

The examples suggested in the lecture of quantities which are discontinuous at a boundary do fail to give exact differentials. However, they violate the conditions about continuity of F or its first derivatives rather than the symmetry of mixed partial derivatives. *It is hard to find examples of functions which violate this condition.*

A.2 Inexact differentials

An inexact differential is in some sense the opposite of an exact differential.

Definition A.2. *An inexact differential $đF$ is a differential for which no function F satisfies*

$$F = \int đF. \tag{A.4}$$

They are differentials which cannot be integrated. In thermodynamics the most common examples are the work and the heat expressed as

$$đW = -PdV, \tag{A.5}$$

$$đQ = TdS. \tag{A.6}$$

---

[38]Found here `https://en.wikipedia.org/wiki/Symmetry_of_second_derivatives`.

One way to realise that these are not exact is to consider them as parts of the exact differentials

$$d\left(-PV\right) = -VdP - PdV, \tag{A.7}$$
$$d\left(TS\right) = TdS + SdT. \tag{A.8}$$

We will see both of these exact differential when transforming between the different thermodynamic potentials in later lectures.

The classical mechanics example that I gave, $dW = \vec{F} \cdot d\vec{x}$ is useful to have in mind. It highlights that if F is conservative, i.e $\vec{F} = \nabla V$, then we can integrate $-\vec{F} \cdot d\vec{x}$ to find the potential energy V. This is because we can integrate the components of $\vec{F}$ in a consistent way so that the same V differentiates to all of them.

Example A.3. Consider the force $\vec{F} = -\left(x\hat{x} + y\hat{y} + z\hat{z}\right) = -\vec{r}$. This is a conservative force[39] and we find V in the following way: Compute

$$\int F_x dx = -\frac{x^2}{2} + C(y, z), \tag{A.9}$$

$$\int F_y dy = -\frac{y^2}{2} + C(x, z), \tag{A.10}$$

$$\int F_z dz = -\frac{z^2}{2} + C(x, y). \tag{A.11}$$

The "constant" terms are only constant with respect to the variable that is integrated over. If $\vec{F} = -\nabla V$ then $dV = \nabla V \cdot dx = -\vec{F} \cdot d\vec{x}$ and V is found from

$$V = -\int F_x dx - \int F_y dy - \int F_z dz = \frac{r^2}{2} - C(y, z) - C(x, z) - C(x, y). \tag{A.12}$$

The constant pieces are found by checking ∇V is consistent with the given vector $\vec{F}$:

$$C(y, z) = \text{constant}, \tag{A.13}$$
$$C(x, z) = \text{constant}, \tag{A.14}$$
$$C(x, y) = \text{constant}. \tag{A.15}$$

During this module you should acquire more experience with inexact differentials.

A.3   Examples

Here are some simple examples of exact and inexact differentials and how to check.

Example A.4. The differential $df = xdx + ydy$ is an exact differential as

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = 0, \tag{A.16}$$

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = 0 \tag{A.17}$$

agree.

---

[39]Feel free to compute that $\nabla \times \vec{F} = 0$ to check the PY2101 condition for conservative forces.

Example A.5. $du = 2ydx + xdy$ is an inexact differential. If it was exact then we could write

$$\frac{\partial u}{\partial x} = 2y, \tag{A.18}$$

$$\frac{\partial u}{\partial y} = x. \tag{A.19}$$

However, this leads to the mixed partial derivatives

$$\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial x}\right) = 2, \tag{A.20}$$

$$\frac{\partial}{\partial x}\left(\frac{\partial u}{\partial y}\right) = 1 \tag{A.21}$$

which do not agree.

Example A.6. The differential $df = ydx - xdy$ is not an exact differential as

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = 1, \tag{A.22}$$

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = -1 \tag{A.23}$$

which do not agree.

B Mathematical Identities

This appendix is a list of useful mathematical identities that are needed in the main body of the lecture notes.

B.1 Useful Integrals

This is mostly a reproduction of Appendix C of [Gue07].

Example B.1. Maxwell-Boltzmann Integrals

$$I_n = \int_0^\infty y^n \exp\left(-by^2\right) dy \tag{B.1}$$

There are three cases involved in evaluating this:

1. $I_0 = \frac{1}{2}\left(\frac{\pi}{b}\right)^{\frac{1}{2}}$.

2. $I_1 = \frac{1}{2b}$.

3. For $n \geq 2$ we have the recurrence relation $I_n = \left(\frac{n-1}{2b}\right) I_{n-2}$. Using this every integral with the form of Equation. (B.1) to a multiple of either I_0 or I_1.

Example B.2. Fermi-Dirac Integrals

It is frequently necessary to approximate integrals involving the Fermi-Dirac distribution $f(\varepsilon)$. These integrals typically have the form

$$I = \int_0^\infty \frac{dF(\varepsilon)}{d\varepsilon} f(\varepsilon)\, d\varepsilon, \tag{B.2}$$

with $F(\varepsilon)$ a function specific to each occurrence of this integral. Close to $\varepsilon = \mu$ this can be approximated as

$$I = F(\mu) + \frac{\pi^2}{6} (k_B T)^2 F''(\mu) + \dots. \tag{B.3}$$

The coefficient of the second derivative term is found from

$$\int_0^\infty \frac{y^2 e^y}{(1 + e^y)^2} dy = \frac{\pi^2}{6}. \tag{B.4}$$

References

[AM20] N. Ashcroft and N. Mermin. *Solid State Physics*. Cengage Learning, Incorporated, 2020.

[Atk07] P. Atkins. *Four Laws That Drive the Universe*. Very Short Introductions. OUP Oxford, 2007.

[Fey98] R.P. Feynman. *Statistical Mechanics: A Set Of Lectures*. Advanced Books Classics. Avalon Publishing, 1998.

[Gue07] A.M. Guenault. *Statistical Physics*. Student Physics Series. Springer Netherlands, 2007.

[KK80] C. Kittel and H. Kroemer. *Thermal Physics*. W. H. Freeman, 1980.

[LLP80] L.D. Landau, E.M. Lifshitz, and L.P. Pitaevskii. *Course of Theoretical Physics: Statistical Physics, Part 2 : by E.M. Lifshitz and L.P. Pitaevskii*. Number v. 9. 1980.

[Man71] F. Mandl. *Statistical Physics*. Manchester physics series. Wiley, 1971.

[SS75] F.W. Sears and G.L. Salinger. *Thermodynamics, Kinetic Theory, and Statistical Thermodynamics*. Addison-Wesley principles of physics series. Addison-Wesley Publishing Company, 1975.