PHYS20352 Statistical Physics
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Contents

Chapter 1

Revision of thermodynamics

In this chapter, the reader is referred to sections 1 & 2 of the on-line notes of the previous version of this course for more details and references.

1.1 States of a system

Take-home message: Classical thermodynamics describes macroscopic systems in equilibrium in terms of a few measurable variables

Thermodynamics as you studied it last year is largely a study of *macroscopic systems* in, or approximately in, *equilibrium*. Mostly these were fluids, particularly gases, and "macroscopic" refers to the fact that we were dealing with reasonably large quantities, measured in moles and grams. Empirically, when such a system is allowed to reach thermal and mechanical (and if necessary chemical) equilibrium, it is described by a very few properties such as temperature, pressure, volume and composition (if more than one species is present). These properties are termed *functions of state* or *state variables*, as it is empirically observed that they are determined only by the present state of the system and not the history by which it reached that state. Furthermore though one can add a few further state variables to the list, such as internal energy and entropy, it turns out that they cannot all be varied independently. For a given mass of a single-component fluid, for instance (not necessarily an ideal gas), if the temperature and pressure are specified, everything else has a definite value which cannot be altered. Relationships between these variables (which may or may not have a simple form) are called *equations of state.*

Equilibrium is in practice never absolute: the most stable gas in the most unreactive vessel will still eventually leak out or distort or corrode its container. But for all practical purposes, we can talk about it being in equilibrium once there is no net observable flow of particles or heat between different regions of the system. Gases come to equilibrium very quickly on a human times scale; treacle rather less quickly. Some systems "never" do, it seems; glasses are an example. Systems that exhibit *hysteresis* (dependence on past conditions, such as permanent magnets) do not reach equilibrium in a reasonable time. But in this lecture course we will assume that for systems of interest equilibrium can be reached, and that changes to the conditions (eg pressure) can be made sufficiently slowly that the system remains in equilibrium (sometimes termed "quasi-equilibrium") at all times. A *reversible* process is one in which an infinitesimal change in the external conditions is enough to reverse the direction of the process; an example would be the compression of a gas in a cylinder with a frictionless piston by exerting an external force only just sufficient to move the piston one way or the other. When we draw the reversible compression of a gas on a PV plot, we are assuming that the system always has a well-defined pressure, which would not be the case if there were turbulence or shock waves arising from too-rapid movement of the piston. Such irreversible processes are drawn as dotted lines between the initial and final states.

In the context of these lectures, the state of a macroscopic system in equilibrium specified by a handful of macroscopically-manipulable variables is call the *macrostate*. It completely ignores what is going on with the very many individual atoms that comprise the system. A much richer description of the positions and momenta of all the atoms (or of their combined quantum state) is in principle possible, and it is called a *microstate* of the system.[1] The ability of classical thermodynamics to describe systems without reference to the microstates is a consequence of the laws of probability and of large numbers. The goal of statistical physics is to derive thermodynamics from the behaviour of atoms and molecules, and we will returmn to this in the next chapter. The current chapter is largely revision of ideas already met in Properties of Matter.

1.2 The Zeroth Law of Thermodymamics

Take-home message: Absolute zero is the point at which thermal motion of an ideal gas vanishes

The *zeroth law of thermodynamics* says that if two bodies are separately in thermal equilibrium with a third body, they are also in thermal equilibriums with one another. All three are then said to be at the same temperature.

If the third body changes visibly as it is heated, then it can be used as a “thermoscope” to verify equality of temperature or to rank bodies according to temperature. This is independent of any numerical scale.

A **thermometer** is a calibrated thermoscope. Any thermoscope can be used to define a numerical temperature scale over some range. Thermoscopes based on the volume of gases led finally to the **ideal gas or absolute** temperature scale, measured in Kelvin and defined to be 273.16 K at the triple point of water:

$$T = \lim_{P\to 0} \frac{PV}{(PV)_{\text{triple}}} \times 273.16\ \text{K} \tag{1.1}$$

The low pressure limit is taken because real gases approach ideal behaviour in that limit. The numerical value at the triple point was chosen so that the degree Kelvin matched the degree Celsius to high accuracy. Unlike earlier temperature scales there is no need to define the temperature at two points, because the zero of the Kelvin scale is absolute zero. This is the temperature at which the pressure of an ideal gas would vanish, because (classically) the motion of its molecules would cease.

In these notes, the symbol T will always refer to absolute temperature.

1.3 Internal energy
and the First Law of Thermodynamics

Take-home message: Energy can be transferred to a system by adding heat or doing work, but the net effect is the same

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[1] A microstate is NOT necessarily the state of a microscopically small system! Systems of any size have microstates, though only large systems also have macrostates.

The *first law of thermodynamics* states that any change in internal energy E of a system is due to the amount of heat added to it and the work done on it:

$$\Delta E = Q + W \qquad \text{or} \qquad \mathrm{d}E = đQ + đW \tag{1.2}$$

The internal energy is a function of state and changes by a finite (ΔE) or infinitesimal ($\mathrm{d}E$) amount in any process. But heat and work are NOT functions of state; the same change of state may be effected by different reversible or irreversible processes involving different amounts of heat transfer and work done. $đQ$ and $đW$ are not true differentials but just infinitesimal amounts of energy transfer in the form of heat and work.

For reversible processes we write

$$\mathrm{d}E = đQ^{\text{rev}} + đW^{\text{rev}} \tag{1.3}$$

In an *adiabatic* processe, $Q = 0$.

For a system taken round a cycle, so that it returns to its initial state, it is obvious that $\Delta E = 0$. But Q and W, not being functions of state, will not vanish in general. This is the basis of a heat engine: the net work done by the system is equal to the net heat transferred to the system. But we will see in a moment that one cannot simply add an amount of heat and extract the same amount of work. Some of the heat must be discarded.

Expressions for the work done in reversible processes are as follows:
Compression of a fluid

$$đW^{\text{rev}} = -P\,\mathrm{d}V \tag{1.4}$$

To reversibly stretch a wire of tension Γ (that's a capital gamma) by $\mathrm{d}l$ requires

$$đW^{\text{rev}} = \Gamma\,\mathrm{d}l \tag{1.5}$$

and to increase the area of a film of surface tension γ by $\mathrm{d}A$ requires

$$đW^{\text{rev}} = \gamma\,\mathrm{d}A \tag{1.6}$$

Note in the last two cases the sign is different from the first; that's because it takes work to *stretch* a wire or a soap film ($\mathrm{d}l$ or $\mathrm{d}A$ positive) but to *compress* a gas ($\mathrm{d}V$ negative).

Lastly, to reversibly increase the magnetic field B imposed upon a paramagnetic sample requires

$$đW^{\text{rev}} = -\mathbf{m}\cdot\mathrm{d}\mathbf{B} = -V\mathbf{M}\cdot\mathrm{d}\mathbf{B} \tag{1.7}$$

where $\mathbf{M}$ is the magnetisation per unit volume, and $\mathbf{m}$ is the total magnetic moment of the sample.

To repeat, these hold only for reversible processes. To calculate the internal energy change for irreversible processes such as the free expansion of a gas, it is necessary to find a reversible process linking the same initial and final states of the system.

1.4 Second law of Thermodynamics

Take-home message: No process which would decrease the entropy of a system will happen spontaneously. OR Heat won't pass from a cooler to a hotter; You can try it if you like but you far better notter

It is observed that when systems start out of equilibrium, they always evolve to the same equilibrium state determined by the external constraints. For instance if a gas is isolated from its surrounding in an insulating container and is initially confined only to one part of that container, if it is then allowed to spread to the whole container it will always reach the same, uniform, state. (Note that to even talk of a system being out of equilibrium there has to be something about the system which is NOT specified by the functions of state such as internal energy and total container volume; here it includes the relative amount of gas in different parts of the container.) Or if two bodies not at the same temperature are brought into thermal contact, heat will flow from the hotter to the cooler till they end up at the same temperature and not evolve further. Heat will never be observed to flow from in the other direction.

It is also observed that in any process that extracts energy from an out-of-equilibrium system (such as a hot body with colder surroundings) in order to do work, it is not possible to use all of the energy that would flow to the surroundings if it were left to cool naturally. Some (in practice most) of the energy will always need to be discarded to the surroundings as waste heat.

These two observations are summarised in two statements of the second law of thermodynamics

There are two classic statements of the **second law of thermodynamics**

One due to **Kelvin and Planck**:

> It is impossible to construct an engine which, operating in a cycle, will produce no other effect than the extraction of heat from a reservoir and the performance of an equivalent amount of work.

And another due to **Clausius**:

> It is impossible to construct an refrigerator which, operating in a cycle, will produce no other effect than the transfer of heat from a cooler body to a hotter one.

Note the careful wording: of course it is possible to think of processes which convert heat into work (expansion of a hot gas in a piston) or which pass heat from a cool to a hot body (real fridges) but other things change as well (the gas ends up cooler; you have an electricity bill to pay). The bit about "operating in a cycle" ensures that the engine is unchanged by the process.

The two statements may not appear to have anything to do with one another, but in fact each one implies the other: a hypothetical engine or pump which violates one statement can, along with another normal engine or pump, form a new composite machine which violates the other.

Clausius's statement leads to the following. By consideration of a system taken round a cycle, with heat added to and removed from the system while it or the relevant part of it is at various temperatures, Clausius's theorem says that the sum of the heat added weighted by the inverse of the temperature at which it is added is less than or equal to zero:

$$\oint \frac{đQ}{T} \leq 0 \tag{1.8}$$

The inequality becomes an equality for reversible systems, for which we could take the cycle in the opposite direction:

$$\oint \frac{đQ^{\text{rev}}}{T} = 0. \tag{1.9}$$

This is interesting because a quantity whose change vanishes over a cycle implies a function of state. We know that heat itself isn't a function of state, but it seems that in a reversible process "heat over temperature" **is** a function of state. It is called *entropy* with the symbol S:

$$dS = \frac{đQ^{\text{rev}}}{T} \tag{1.10}$$

Hence we have, for a fluid, a new statement of the first law: the fundamental thermodynamic relation

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V \tag{1.11}$$

Note that reversible adiabatic processes are isentropic and $\mathrm{d}E = đW^{rev}$.

Furthermore, by considering a cycle in which a system undergoes an irreversible change, followed by a reversible return to the initial state, we have

$$đQ^{\text{irrev}} < T\mathrm{d}S \tag{1.12}$$

and so, for an isolated system, during any spontaneous change

$$\mathrm{d}S \geq 0. \tag{1.13}$$

and once the entropy reaches a maximum, no further change can take place and the system is in equilibrium.

An alternative statement of the second law is thus:

The entropy of an isolated system can never decrease.

This is a powerful principle, but it is empirically based and leaves many questions unanswered, principally about the nature of entropy.

If we start with entropy increase, we recover Clausius' statement: when a (positive) amount of heat Q flows from a hotter body to a cooler one, the entropy decrease of the hot body, $-Q/T_H$ is less than the entropy increase of the cold body, Q/T_C. So overall the entropy of the hot and cold bodies together (or a hot body plus its cooler surroundings, together "the universe") increases.

We also recover Kelvin's statement: to remove heat from a hot body and turn it entirely into work will decrease the entropy of the universe. We need to add enough of the heat to the surroundings so that their entropy increases to compensate.

In a Carnot engine Q_H is removed from a hot reservoir and Q_C is discarded to a cold one in such a way that the combined entropy change is zero

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C} \tag{1.14}$$

and the difference is available to do work: $W = Q_H - Q_C$.

Along with heating, other processes which increases entropy are free expansion of a gas, or mixing of two species of gas initially confined to different parts of a chamber. It is not immediately clear what these have in common....

1.5 Thermodynamic potentials

Take-home message: Depending on the external conditions, other "potentials" or "free energies" are easier to work with than the internal energy as they account for the entropy changes of the surroundings

The **fundamental thermodynamic relation**

$$\mathrm{d}E = T\mathrm{d}S - P\mathrm{d}V \tag{1.15}$$

implies that there is a function $E(S,V)$ with

$$\left.\frac{\partial E}{\partial S}\right|_V = T \qquad \text{and} \qquad \left.\frac{\partial E}{\partial V}\right|_S = -P \tag{1.16}$$

Equivalently we may use $S(E,V)$:

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + \frac{P}{T}\mathrm{d}V; \qquad \left.\frac{\partial S}{\partial E}\right|_V = \frac{1}{T} \qquad \text{and} \qquad \left.\frac{\partial S}{\partial V}\right|_E = \frac{P}{T} \tag{1.17}$$

In this view, temperature and pressure are derived properties of systems whose energy and volume are fixed. This is appropriate for isolated systems.

However in practice we often want to work with temperature as the variable we control, and systems which are not isolated but in contact with a heat bath of our choice.

Now we cannot say that the approach to equilibrium will maximise the entropy of the system, because it can exchange heat with the heat bath at temperature T, and only when we consider both together will entropy increase.

Imagine a spontaneous change at constant volume during which Q is absorbed by the system, $\Delta E = Q$. The system starts and ends at the temperature T of the heat bath, though it may change in between (due to a chemical reaction, for instance). The total change in entropy has two parts, ΔS for the system and $-Q/T$ for the surroundings. So

$$\begin{aligned} \Delta S_{\text{tot}} = \Delta S - \frac{Q}{T} &= \frac{1}{T}(T\Delta S - \Delta E) \geq 0 \\ \Rightarrow \quad & \Delta(TS - E) \geq 0 \end{aligned} \tag{1.18}$$

So if we concentrate only on the system, rather than its entropy being maximised in the approach to equilibrium, the quantity $TS - E$ is maximised. Conventionally we define the Helmholtz free energy, F, as the negative of this, so it is minimised. We have

$$F = E - TS \qquad \Rightarrow \qquad \mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V; \tag{1.19}$$

and

$$\left.\frac{\partial F}{\partial T}\right|_V = -S \qquad \text{and} \qquad \left.\frac{\partial F}{\partial V}\right|_T = -P. \tag{1.20}$$

The Helmholtz free energy will turn out to play a crucial role in statistical physics.

If we fix the pressure rather than the volume, we are led to define

$$G = E - TS + PV \qquad \Rightarrow \qquad \mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P; \tag{1.21}$$

and the approach to equilibrium minimises the Gibbs free energy G of the system.

In the latter two cases, the principle is still that the system plus surroundings together evolve to maximise their entropy. It only looks as if the system may be "trying to minimise its energy" because an energy transfer to (possibly cooler) surroundings more than compensates for the decrease in entropy of the system itself.

1.6 Variable particle number

Take-home message: The chemical potential is the same as the Gibbs free energy, and it is the key to diffusive and chemical equilibrium

In all of the above we have assumed a fixed amount of material in the system. If however it is in diffusive contact with a reservoir, we must add a term $+\mu\mathrm{d}N$ to each of $\mathrm{d}E$, $\mathrm{d}F$ and $\mathrm{d}G$. μ is the so-called *chemical potential*, and just as heat flows from high to low temperature, particles flow from high to low chemical potential, and equilibrium—no net flow—means equal chemical potential. One of the three expressions for μ as a derivative of a thermodymamic potential is

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \tag{1.22}$$

But G is extensive, and P and T are intensive, so G must be directly proportional to N: $G(T, P, N) = Ng(T, P)$ (where g is the Gibbs free energy per molecule), and so $\mu = g$. So for a single component system, μ is just the Gibbs free energy per molecule. Phase coexistence at a given temperature and pressure, for instance, requires equal Gibbs free energy per molecule in the two phases. Otherwise the system would evolve to minimise its Gibbs free energy and one phase would convert into the other (melt, freeze, boil, condense....).

However for a two-component system, with separate chemical potentials μ_1 and μ_2, G depends not only on the extensive variable $N = N_1 + N_2$ but also on the *ratio* N_1/N_2, which is intensive. The Gibbs free energy per molecule of one substance can depend on the concentration of the other. If substance 1 is ethanol and substance 2 water, the chemical potential of ethanol is different in beer (5%) and vodka (40%). None-the-less an extension of extensivity—that G must double if N_1 and N_2 both double—can be shown, rather surprisingly, to imply that

$$G = \sum_i \mu_i N_i. \tag{1.23}$$

In other words the chemical potential of each species remains the Gibbs free energy per particle of that species, even though it also depends on the relative concentrations of all species present.[2]

For an ideal gas,

$$S(T, P) = S(T_0, P_0) + C_p \ln\frac{T}{T_0} - nR\ln\frac{P}{P_0}. \tag{1.24}$$

At constant temperature T_0, E and PV are also constant, and so from $G = E - TS + PV$ we have an expression comparing the chemical potential or Gibbs free energy per molecule at two different pressures:

$$\mu(T_0, P_2) - \mu(T_0, P_1) = k_B T_0 \ln\frac{P_2}{P_1} \tag{1.25}$$

For mixtures of ideal gases, the absence of interactions means that each species has the same chemical potential as it would if the other species were absent, and hence the pressure were equal to the *partial pressure* of that species, $P_i = (N_i/N)P$.

Eq. (1.25) says the chemical potential is higher at higher pressures and gas will diffuse from higher to lower pressure. (A similar expression holds for solutions, with pressure replaced by concentration.) That seems obvious, but it *is* different from the equalisation of mechanical pressure. In particular if two ideal gases are at different concentrations on either side of a rigid membrane, but only one can pass through, the partial pressure of the mobile one will equalise even if that increases the mechanical total pressure on one side.

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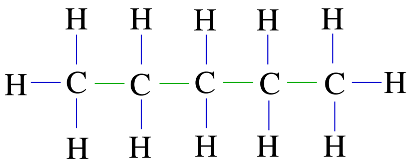
[2] We will prove this when we consider the Grand Potential later in the course, see section 3.14.

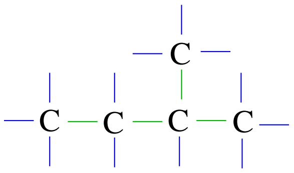
1.6.1 Chemical Reactions

The treatment of chemical reactions is very like that of phase transitions. Again, we are considering conditions of constant temperature and pressure, and the question is the following: how far will a reaction go?

First consider the simplest case of a reaction with only one reactant and one product: A $\rightleftharpoons$ B. An example is the interconversion of n-pentane and isopentane (or pentane and methyl-butane, for those of us who learned our chemistry in the last fifty years).



pentane



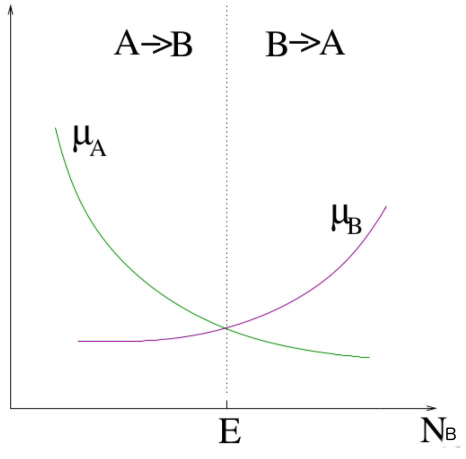
methylbutane

(hydrogens omitted)

Spontaneous changes will minimise the Gibbs free energy. With temperature and pressure fixed only the numbers of A and B can change. Since they can only interconvert, $\mathrm{d}N_A = -\mathrm{d}N_B$ and

$$\mathrm{d}G = \mu_A\,\mathrm{d}N_A + \mu_B\,\mathrm{d}N_B = (\mu_A - \mu_B)\mathrm{d}N_A \tag{1.26}$$

So if $\mu_A > \mu_B$, A will convert to B, but if $\mu_B > \mu_A$, the opposite will happen. So at equilibrium, when no further changes happen, the chemical potentials must be equal. (Remember that the chemical potentials are functions of concentration, so they will change as the reaction proceed.)



In the figure "E" marks the equilibrium concentration, at the point where $\mu_A = \mu_B$.

If there are more reactants or products, say for the more general reaction in which a moles of A and b moles of B react to form x moles of X and y moles of Y,

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons x\mathrm{X} + y\mathrm{Y}, \tag{1.27}$$

the numbers of A, B, X and Y change together: $\mathrm{d}N_A = (a/b)\mathrm{d}N_B = -(a/x)\mathrm{d}N_X = -(a/y)\mathrm{d}N_Y$. So

$$\mathrm{d}G = \mu_A\,\mathrm{d}N_A + \mu_B\,\mathrm{d}N_B + \mu_C\,\mathrm{d}N_C + \mu_D\,\mathrm{d}N_D = \tfrac{1}{a}(a\mu_A + b\mu_B - x\mu_X - y\mu_Y)\,\mathrm{d}N_A \tag{1.28}$$

and equilibrium is when

$$a\mu_A + b\mu_B = x\mu_X + y\mu_Y. \tag{1.29}$$

This result is general: equilibrium is reached when the weighted sum of the chemical potentials of the reactants equals that of the products.

Now consider the hugely simplified case where the species are in gaseous form and can be treated as ideal gases, so that their chemical potential is just their Gibbs free energy per mole, $\mu_i = g_i(P_i, T)$. (Here g refers to G/n rather than G/N.)[3]

We define the molar Gibbs free energy of reaction as

$$g_r = xg_X + yg_Y - ag_A - bg_B \tag{1.30}$$

and this will be zero at equilibrium. If we know $g_r^0 \equiv g_r(T_0, P_0)$ at some reference temperature and the same reference partial pressure for all reactants and products, (usually $T_0 = 25^{\circ}\mathrm{C}$ and $P_i = P_0 = 1$ bar), then at other partial pressures but the same temperature, from (1.25) it will be

$$\begin{aligned} g_r(P_i, T_0) =& g_r^0 + RT_0\left(x\ln\frac{P_X}{P_0} + y\ln\frac{P_Y}{P_0} - a\ln\frac{P_A}{P_0} - b\ln\frac{P_B}{P_0}\right) \\ =& \, g_r^0 + RT_0\ln\left[\left(\frac{P_X}{P_0}\right)^x\left(\frac{P_Y}{P_0}\right)^y\left(\frac{P_0}{P_A}\right)^a\left(\frac{P_0}{P_B}\right)^b\right] \end{aligned} \tag{1.31}$$

Hence, since at equilibrium $g_r = 0$,

$$\left(\frac{P_X}{P_0}\right)^x\left(\frac{P_Y}{P_0}\right)^y\left(\frac{P_0}{P_A}\right)^a\left(\frac{P_0}{P_B}\right)^b = \exp\left(-\frac{g_r^0}{RT_0}\right) = K_p(T_0)\,. \tag{1.32}$$

If $g_r^0 < 0$ and so K is large, the reaction will tend to favour the products (X, Y) over the reactants (A, B); if on the other hand $g_r^0 > 0$ (K small) the reactants will be favoured, But the actual composition at equilibrium will depend on the initial conditions; if for instance B is in very short supply, there will always be plenty of A left. If the LHS of equation (1.32) is calculated for some non-equilibrium state it is called Q; the reaction will go forwards if $Q < K$ and backwards if $Q > K$.

Chemists know $K_p(T)$ as the equilibrium coefficient, and using the symbol [A] for the ratio of the concentration of species A in a gas or liquid to a standard concentration, write (1.32) as

$$\frac{[\mathrm{X}]^x[\mathrm{Y}]^y}{[\mathrm{A}]^a[\mathrm{B}]^b} = K_c(T). \tag{1.33}$$

The two equilibrium constants are not numerically the same, because they refer to different standard states ($n_0 = 1$ mol l^{-1} for concentrations). They are related by

$$K_p = (n_0RT/P_0)^{x+y-a-b}K_c. \tag{1.34}$$

We have predicted K_p for ideal gases and solutions, but only in terms of a known Gibbs free energy of reaction at that temperature and standard pressures/concentrations. To predict the behaviour as a function of temperature requires the statistical theory.

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[3] This is the only section in which we will use g to mean specific Gibbs free energy. In statistical physics g will always be a degeneracy factor, the number of microstates with the same energy.

For completeness, the general forms of these equations for N reactants and N' products can be written

$$g_r = \sum_{i=1}^{N'} x_i g_{X_i} - \sum_{j=1}^{N} a_j g_{A_j} \tag{1.35}$$

and, at equilibrium,

$$\prod_{i=1}^{N'} \left(\frac{P_{X_i}}{P_0}\right)^{x_i} \prod_{1=1}^{N} \left(\frac{P_0}{P_{A_j}}\right)^{a_j} = \exp\left(-\frac{g_r^0}{RT_0}\right). \tag{1.36}$$

Note, as given, g_r will depend on whether the reaction is written, e.g., $O_2 + 2H_2 \rightleftharpoons 2H_2O$ or $\frac{1}{2}O_2 + H_2 \rightleftharpoons H_2O$, being twice as large in the first case as in the second. You should be able to convince yourself that the partial pressures at equilibrium do not depend on this. For a reaction with a single product like this one, though, it is usual to talk about the standard Gibbs free energy of formation as referring to a single mole of product, i.e. the second case.

All of this is phrased in terms of chemical reactions. But not all reactions are chemical: in a neutron star, neutrons, protons and electrons can interact via $\mathrm{p} + \mathrm{e}^- \rightleftharpoons \mathrm{n}$; they reach an equilibrium at which the chemical potentials on either side of the reaction are equal. This is heavily biased toward neutrons, because the chemical potential of the light electron is much higher for a given concentration than that of the heavy proton or neutron. The treatment above doesn't reveal that, it would be hidden in the reference quantity g_r^0. But in fact, we can and will demonstrate it in statistical physics.

Chapter 2

Statistical Physics of isolated systems

Take-home message: We hope to answer the following questions - what is entropy? why does it increase? can we predict the equations of state of a system from first principles?

References

- **Mandl** 2.1-2
- **Bowley and Sánchez** 4.1 (beware–B&S use W for Ω)
- **Kittel and Kroemer** 1,2

The heart of the method of Statistical Physics is to predict the macroscopic properties of a system in equilibrium by averaging over all the microstates which are compatible with the constraints—fixed volume, energy and particle number for an isolated idea gas in a perfectly insulating container, for instance, or (in subsequent sections) fixed temperature and chemical potential instead of energy and particle number. Furthermore we have to assign a value for the probability with which each microstate should contribute to the average. The set of all allowed microstates is called an *ensemble* and the averages are ensemble averages.

When we measure the properties of a gas, we know instinctively that the momentary positions and momenta of all the particles are not important. They are changing constantly on a timescale which is very short compared with the time it takes to make any measurement of pressure, temperature etc. If the average time between collisions is of the order of nanoseconds, and if there are 10^{23} atoms in a container, the state of the system changes 10^{32} times per second! What we measure really is some kind of time-averaged effect of many microscopic motions. (Think of the kinetic theory derivation of pressure, for instance.) Statistical Physics formalises this, and says that for an isolated system we will obtain the correct macroscopic result if we take an ensemble average over all accessible microstates, *assigning them equal probability.* This would be justified in classical mechanics if something called the *ergodic hypothesis* were true: this states that the during its time evolution, a system visits all possible accessible states in phase-space (specified by the positions and momenta of all particles) with equal probability.

A whole branch of mathematics is devoted to the ergodic hypothesis in systems which include, but are not restricted to, Newtonian dynamics. Some flavour of the topic may be covered in the third year course on non-linear systems. But we are not going to explore it here. Quite apart from anything else, we know that quantum, not classical, mechanics, is the correct paradigm, and will be important for many of the systems we will look at. We will briefly consider the ideal gas in classical mechanics, largely for historical interest. However we will not start with a gas, but with something much easier to picture, something with a close analogue in a simple counter problem: the ideal paramagnetic lattice.

2.1 Microcanonical Ensemble

Take-home message: The properties of a macrostate are averaged over many microstates.

The crucial link from microscopic to macroscopic properties is as follows. If the value of some quantity X in the ith microstate is X_i, and the probability that the system is in that microstate is p_i, then the value of X in the macrostate is the **ensemble average**.

$$\langle X \rangle = \sum_i p_i X_i \tag{2.1}$$

An ensemble is just a collection: we imagine a collection of copies of the system, each in one of the allowed microstates. If the number of copies ν is much, much larger than Ω, then each microstate will be represented with a frequency which reflects its probability: if ν_i is the number of copies in state i, we have $\nu_i = \nu p_i$. (We use ν for numbers of copies, and n or N for numbers of atoms. The former is hugely greater than the latter—it is just as well that it is only a theoretical concept.)

Then if we use $\lambda = 1 \dots \nu$ to label the copies and i to label the microstates,

$$\langle X \rangle = \frac{1}{\nu} \sum_\lambda X_\lambda = \frac{1}{\nu} \sum_i \nu_i X_i = \sum_i p_i X_i \tag{2.2}$$

There are three kinds of ensembles commonly used in statistical physics. Where the real system is **isolated**, that is at fixed energy and particle number, the copies in the ensemble are also isolated from one another; this is called the **microcanonical ensemble**.

If the real system is in contact with a **heat bath**, that is at fixed **temperature**, the copies are assumed to be in thermal contact, with all the rest of the copies acting as a heat bath of any individual copy. This is called the **canonical ensemble**.

Finally, if the real system can exchange both heat and particles with a reservoir, at fixed **temperature and chemical potential**, the copies are also assumed to be in diffusive contact. This is called the **grand canonical ensemble**.

The idea that averaging over very many copies of a probabilistic system gives, as the number tends to infinity, a fixed reproducible result, is an example of the law of large numbers. As an example, if we roll many identical dice (or one die many times) the average score is predictable (though it is only 3.5 if the die is fair). Though it sounds obvious, in probability theory it does need proved, though we will not do so here. Crucial is the fact that each roll of the die is independent of the others, so that in the jargon the results are "independent identically-distributed random variables". The usual laws of probability say that the probabilities of a set of independent outcomes is just the product of the individual probabilities, so that for instance, with a fair die, the probability of getting first a 6, then anything but a six, in two consecutive rolls is just $\frac{1}{6} \times \frac{5}{6}$.

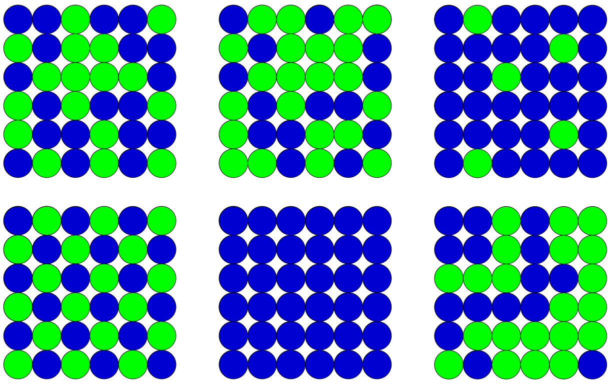
We start by considering an isolated system (constant energy, volume and particle number). The fundamental principle that allows the averaging over microstate to be done is the **postulate of equal *a priori* probabilities** or, in plain English, the assumption that all allowed microstates are equally likely. (Allowed or accessible means having the same volume, particle number and and total energy as the macrostate.) We use Ω for the number of such microstates, so the probability of the system being in any one microstate is

$$p_i = \frac{1}{\Omega} \qquad \text{and} \qquad \sum_i p_i = \Omega \frac{1}{\Omega} = 1 \tag{2.3}$$

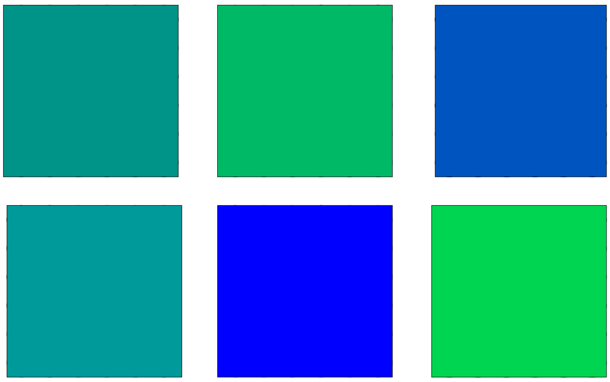
It should be stressed that, as the name suggests, this postulate is not proved. It is assumed to be true, but the validation relies on the success of the predictions of the theory.

Imagine we have counters, blue on one side and green on the other, and we toss them and place them on a 6 × 6 checkerboard. Full information involves listing the colour at each site: this is the equivalent of a microstate.

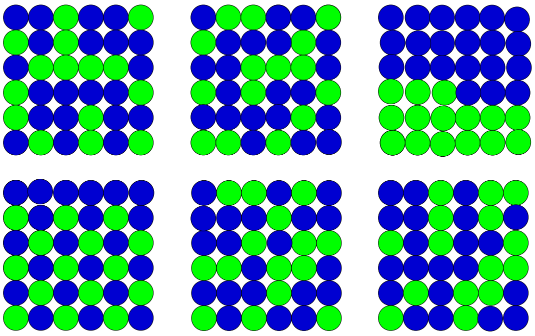
Many different patterns are possible, such as the following. Every configuration is equally likely—or unlikely—to occur: There are $\Omega = 2^{36} = 6.87 \times 10^{10}$ patterns and the the probability of each is $(1/2)^{36} = 1.46 \times 10^{-11}$. (This satisfies the "postulate of equal *a priori* probabilities".)



Suppose from a distance we only knew, from the average colour, how many counters were green and how many blue, without being able to distinguish different arrangements of the same numbers of counters. Then a "macrostate" would be characterised simply by the overall hue, determined by the total number of green counters (the rest being blue).



Clearly, most macrostates correspond to many microstates. If the macroscopic description is "15 green", the following are a few of the allowed microstates:



How many are there in total? This is the common problem of splitting a group of N into two smaller groups, of n and $N-n$, without caring about the ordering in each group, and the number of ways of doing it is

$$\Omega = \frac{N!}{n!\,(N-n)!} \tag{2.4}$$

Think of counters on squares: there are $N!$ ways of putting N distinguishable counters on N squares. However if n of the counters are green, there are $n!$ ways of arranging the green counters among themselves without changing the pattern, and $(N-n)!$ ways of arranging the blues.[1]
Here, $N = 36$ and $n = 15$, so the total is 5.59×10^9. For $n = 10$ there are only 2.54×10^8, whereas for $n = 18$, there are 9.08×10^9. This is the maximum.

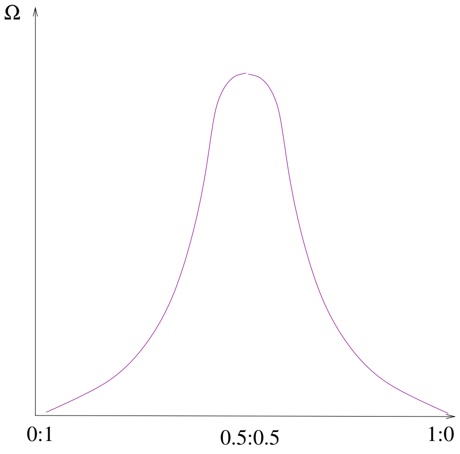
The numbers $N!/n!\,(N-n)!$ are called the *binomial coefficients* (since they enter the binomial expansion) and they are written ${}^N C_n$ or $\binom{N}{n}$.

2.2 The statistical basis of entropy

Take-home message: The increase of entropy can be understood as an evolution from less to more probable configurations

Suppose a system has an extra degree of freedom which isn't specified by fixing the volume and internal energy. For a mixture of two ideal gases, it could be the degree to which they are fully mixed–for example ratio of the concentrations of one species on either side of the box. If the gases started out separated by a partition the concentrations would start at 0:1; the classical law of increase of entropy tells us they will evolve till the ratio reaches 0.5:0.5, and not change thereafter. (You have previously calculated the increase in entropy to be $2nR\ln 2$, for n moles initially in each half of the box.) At the classical level, we don't understand this yet. It is just a law of nature, deduced ultimately from observation.

Statistical physics can explain the spontaneous increase of entropy. There are many more microstates corresponding to the equilibrium configuration (fully mixed) than the non-equilibrium configurations (not fully mixed). The number of microstates as a function of mixing looks something like this, but really much sharper for systems consisting of 10^{23} atoms:



If we start at a point of unequal mixing, the configurations which are rather better mixed are more numerous than those which are rather less well mixed. So as interactions cause the

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[1] Here, there are just two sets of size n and $N-n$. For more sets of size p, q, r....we have $N!/(p!q!r!..)$

system to jump from one microstate to another, it is more likely to end up better mixed. This continues till full mixing is reached, at which point there is no further direction to the changes.

What has this to do with entropy? Classically, the system is evolving from a macrostate of lower entropy to one of higher entropy. Statistically, it is evolving from less probable to more probable macrostates, that is from macrostates corresponding to smaller numbers of microstates to those corresponding to larger numbers of microstates.

So does the number of microstates, Ω, equal the entropy? No, because if we double the size of a system, we have Ω^2, not 2Ω, microstates (think of the number of ways of choosing the microstate of each half independently). So Ω isn't extensive. But $\ln \Omega$ is. So if we make the connection

$$S = k_{B} \ln \Omega \tag{2.5}$$

then we can understand both entropy and its increase.

This expression is due to Boltzmann, it is known as the Boltzmann entropy to distinguish it from a more general expression we will meet later, and it is inscribed on his grave in Vienna (though with W for Ω.)

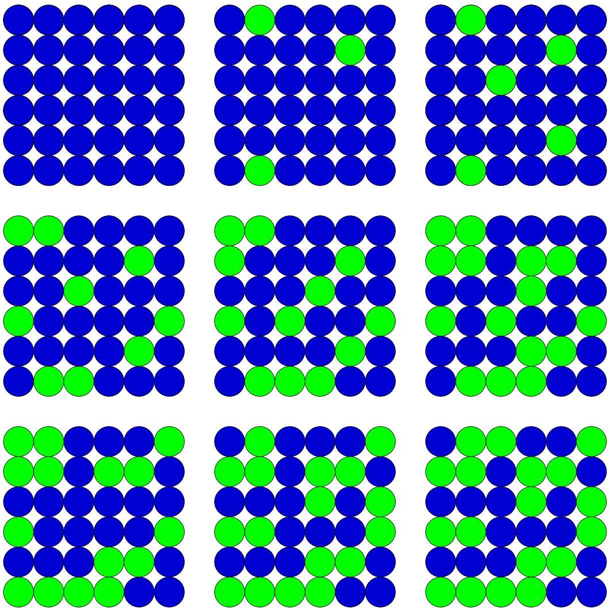
In principle, if the increase of entropy is just a probabilistic thing, it might sometimes decrease. However we will see that for macroscopic systems the odds are so overwhelmingly against an observable decrease that we might as well say it will never happen.

What is k_{B}, Boltzmann's constant? It must be a constant with dimensions of entropy, Joules/Kelvin, and it turns out that the correct numerical correspondence is given by the gas constant R divided by Avogadro's number:

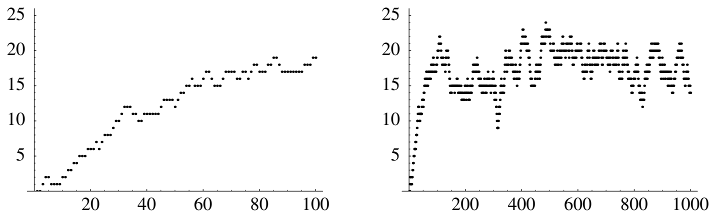
$$k_{B} = \frac{R}{N_{A}} = 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}} = 8.617 \times 10^{-5}\mathrm{eV\,K^{-1}} \tag{2.6}$$

This is validated, for instance, by the derivation of the ideal gas law (see here).

As an example, let's consider the checkerboard example again. Imagine starting with a perfectly ordered all-blue board, then choosing a counter at random, tossing it, and replacing it. After repeating this a few times, there are highly likely to be some green counters on the board—the chance of the board remaining blue is only about 1 in 2^n after n moves. As time goes on, the number of greens will almost certainly increase—not on every move, but over the course of a few moves. Here is a snapshot of the board taken once every 10 moves. The number of greens is 0, 3, 5, 9, 12, 15, 15, 17, 18.

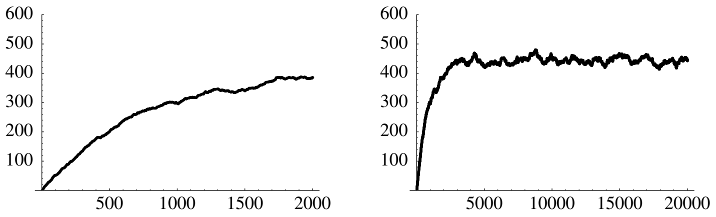


Here is a graph of the number of greens over 100 and 1000 moves.



We see that, after the first 100 moves, the system stayed between 18 ± 6 almost all of the time. These fluctuations are quite large in percentage terms, $\pm 33\%$, but then it is a very small system—not really macroscopic at all.

If we now look at a larger system, 30×30, we see that fluctuations are still visible, but they are much smaller in percentage terms–the number of greens is mostly 450 ± 30, or $\pm 7\%$.



A 25-fold increase in the size of the system has reduced the percentage fluctuations by a factor of 5. We will see later that an n-fold increase should indeed reduce the fluctuations by $\sqrt{n}$. We can predict that a system with 10^{23} counters—truly macroscopic—would have fluctuations of only about $10^{-10}\%$, which would be quite unobservable. The entropy of the system would never appear to decrease.

2.3 The spin-half paramagnet

Take-home message: The paramagnet is the simplest illustration of statistical ideas

- **Mandl** 2.1
- **Bowley and Sánchez** 4.3
- **Kittel and Kroemer** 1,2

What is a spin-$\frac{1}{2}$ paramagnet? A paramagnet is a substance which can be magnetised by an external magnetic field, and the magnetisation is aligned with the external field. Unlike a ferromagnet the response is weak and does not remain if the field is switched off.

A crystal of atoms with non-zero spin will act as a paramagnet, as the spins will tend to line up in an external field. From quantum mechanics we know the spin-projection along the field can only take certain discrete values. For simplicity we consider spin-$\frac{1}{2}$, so that $s_z = \pm\frac{1}{2}$. In an **ideal** paramagnet, the spins do not feel one another, but react independently to an external field.

Thus the ideal paramagnet is a lattice of N sites at each of which the spin points either up or down. Each of these has a magnetic moment $\pm\mu$. Only the total magnetic moment is macroscopically measurable, and this is just the sum of the individual moments. If $n_\uparrow$ spins are pointing up and $n_\downarrow = N - n_\uparrow$ are pointing down, the total magnetic moment is

$$m = n_\uparrow \mu + n_\downarrow(-\mu) = \mu(2n_\uparrow - N). \tag{2.7}$$

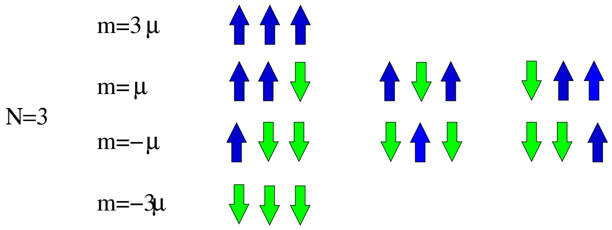
In an external field, the spin-up atoms will have lower energy, $-\mu B$, and the spin-down atoms have higher energy, μB, so the the total energy is just

$$E = n_\uparrow(-\mu B) + n_\downarrow(\mu B) = -Bm \tag{2.8}$$

However we are going to start with **zero external magnetic field** so that all states have the same energy. The magnetisation is then an example of an extra degree of freedom not specified by the energy, as discussed in the previous section.

All the pictures carry over if for "blue" you read spin-up. (The chequerboard is 2-D and a crystal is 3-D, but in the absence of interaction the geometry is irrelevant; all that counts is the total number N of atoms.)

So macrostates are characterised by their magnetic moment (or magnetisation, $M = m/V$), but microstates by the list of spins at each site. For $N = 3$ there are four macrostates and eight microstates.

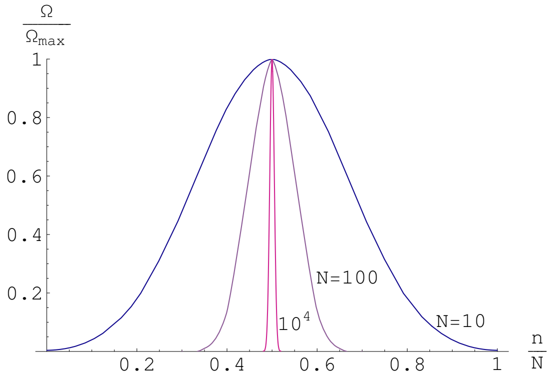


In general the number of microstates for a given macrostate, with $n_\uparrow = \frac{1}{2}(N + m/\mu)$, is

$$\Omega(n_\uparrow) = \frac{N!}{n_\uparrow!\,(N - n_\uparrow)!} \tag{2.9}$$

You should be able to prove that the sum of the $\Omega(N, n_\uparrow)$ over all $n_\uparrow$ is 2^N. (Write $2 = (1+1)\ldots\ldots$)

Below we plot $\Omega(n)$, normalised to 1 at the peak, as a function of n/N, for different values of N.



As N gets larger, the function is more and more sharply peaked, and it is more and more likely that in the absence of an external magnetic field there will be equal numbers of up and down spins, giving zero magnetisation.

For large N, the curve is very well approximated by a Gaussian (see examples sheet),

$$\Omega(n) \propto e^{-\frac{(n-N/2)^2}{N/2}} \tag{2.10}$$

with a mean of $N/2$ and a standard deviation $\sigma = \sqrt{N}/2$. Thus the fractional size of fluctuations goes as $1/\sqrt{N}$.

Since the probabilities of various sizes of fluctuations from the mean in a Gaussian are known, we can show that in a macroscopic system, 100σ deviations are vanishingly unlikely with a probability of 1 in 10^{2173}. Even they would be undetectable (only in part in 10^{10} for a system of 10^{24} particles), so the macroscopic magnetisation is very well defined indeed.

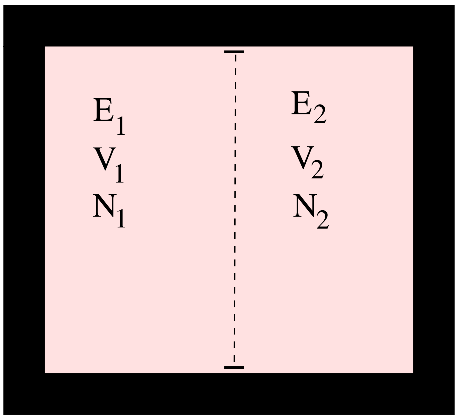
Furthermore the number of microstates of the whole system is dominated by those states where the numbers of up and down spins are approximately equal. In comparison, there are so few of the rest we can ignore them.

The fact that the binomial distribution tends to a Gaussian as the number becomes very large is an example of the *central limit theorem*. It is not restricted to the binomial distribution: for any N independent identically-distributed random variables with mean μ and standard deviation σ, for large N the distribution of their sum is a Gaussian of mean $N\mu$ and standard deviation $\sqrt{N}\sigma$. We won't prove it here, but the examples ask you to test it for a particular example.

2.4 From entropy to temperature

Take-home message: From the entropy, we can calculate all the usual functions of state of a system

- **Mandl** 2.4
- (**Bowley and Sánchez** 2.9)



In the last section we deduced the existence of entropy, and the fact that at equilibrium the entropy is a maximum, from statistical arguments. Now we would like to know if we could go further and, even if we knew no classical thermodynamics, deduce the existence of temperature, pressure and chemical potential.

By considering two systems in contact with one another we can indeed deduce the existence of properties which determine whether they are in thermal, mechanical and diffusive equilibrium even if we knew no classical thermodynamics: these are the three partial derivatives of the entropy with respect to energy, volume and particle number.

Consider a system divided in two by a wall which can move, and through which energy and particles can pass. The equilibrium division of the space into two volumes V_1 and V_2, with energy and particle number similarly divided, will be the one which corresponds to the maximum number of microstates, and hence to the maximum entropy. If we consider heat flow only,

$$\mathrm{d}S = \left(\frac{\partial S}{\partial E_1}\right)_{V_1,N_1} \mathrm{d}E_1 + \left(\frac{\partial S}{\partial E_2}\right)_{V_2,N_2} \mathrm{d}E_2 \tag{2.11}$$

.

But the microstates of each half can be counted independently, so the entropies add:

$$S(E_1, E_2, V_1, V_2, N_1, N_2) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2) \tag{2.12}$$

and also, since the total energy is conserved, $\mathrm{d}E_1 = -\mathrm{d}E_2$. So

$$\mathrm{d}S = \left[\left(\frac{\partial S_1}{\partial E_1}\right)_{V_1,N_1} - \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2,N_2}\right] \mathrm{d}E_1 \tag{2.13}$$

and the entropy will be maximised when a small energy flow no longer changes the entropy:

$$\left(\frac{\partial S_1}{\partial E_1}\right)_{V_1,N_1} = \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2,N_2} \tag{2.14}$$

So we deduce there is some property of bodies which governs heat flow; this is clearly related to temperature. By considering volume changes and particle flow we discover two more properties which are clearly related to pressure and chemical potential. To discover the relation we would have to calculate them for some system and see how they compared with the temperature, pressure etc of classical thermodynamics. However the following assignments clearly work:

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T} \qquad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} \tag{2.15}$$

since they give

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E + \frac{P}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N \tag{2.16}$$

which is the fundamental thermodynamic relation rearranged.

In the following two subsections these ideas are applied to the paramagnet, and we can have our first go at the ideal gas now, too.

2.4.1 The isolated spin-half paramagnet in a magnetic field

We can apply these to the spin-$\frac{1}{2}$ paramagnet in a magnetic field. There is just one difference: we can't derive pressure in this case, because the work is magnetic and not mechanical. Instead of $-P\mathrm{d}V$ we have $-m\mathrm{d}B$ in the fundamental thermodynamic relation, so we have an expression for m instead of P:

$$\frac{m}{T} = \left(\frac{\partial S}{\partial B}\right)_{E,N} \tag{2.17}$$

Now for an isolated system the energy is fixed, and therefore so is the number of up spins: $E = -\mu B(n_\uparrow - n_\downarrow) = \mu B(N - 2n_\uparrow)$ (note μ is now the magnetic moment!) Then we have

$$S = k_{\scriptscriptstyle B} \ln \Omega(E, B) = k_{\scriptscriptstyle B} \ln \left(\frac{N!}{n_\uparrow!\,(N - n_\uparrow)!} \right) \tag{2.18}$$

with $n_\uparrow = \frac{1}{2}(N - E/\mu B)$.

For large numbers of spins, we can use **Stirling's approximation**:

$$\ln n! = n \ln n - n \tag{2.19}$$

giving

$$S = k_{\scriptscriptstyle B} \left(N \ln N - n_\uparrow \ln n_\uparrow - (N - n_\uparrow) \ln(N - n_\uparrow) \right). \tag{2.20}$$

(Note that S is maximum, $S = Nk_{\scriptscriptstyle B} \ln 2$, when $n_\uparrow = n_\downarrow = N/2$, the point of maximum disorder.[2]

So

$$\begin{aligned} \frac{1}{T} &= \left(\frac{\partial S}{\partial E} \right)_{B,N} \\ &= \left(\frac{\partial S}{\partial n_\uparrow} \right)_N \left(\frac{\partial n_\uparrow}{\partial E} \right)_{B,N} \\ &= \frac{k_{\scriptscriptstyle B}}{2\mu B} \ln \left(\frac{n_\uparrow}{n_\downarrow} \right) \end{aligned} \tag{2.21}$$

Differentiating the entropy with respect to B instead, and using the above result for T, we get an expression for m:

$$\frac{m}{T} = -\frac{k_{\scriptscriptstyle B} E}{2\mu B^2} \ln \left(\frac{n_\uparrow}{n_\downarrow} \right) \quad \Rightarrow m = -\frac{E}{B}$$

We knew that of course, but it's good that it works.

We note that for T to be positive there have to be more spins aligned with the field than against it. We will come back to this point later. The paramagnet is unusual in that there is a maximum entropy when $n_\uparrow = n_\downarrow$, corresponding to $T \to \infty$. Most systems can increase their entropy indefinitely as the temperature increases. But for large N, so long as the energy above the ground state E_{excite} is small ($n_\downarrow \ll n_\uparrow$, $E_{\text{excite}} \ll N\mu B/2$), the number of microstates of the paramagnet rises extremely rapidly with energy, and hence the entropy rises too. If we have two paramagnetic samples sharing a fixed energy between them, then the number of microstates of the whole system is $\Omega_{12} = \Omega_1(N_1, E_1)\Omega_2(N_2, E - E_1)$. Ω_1 rises with energy E_1 but Ω_2 falls. The above plot shows the two, together with the number of microstates of the whole system as a function of E_1 (for $N_1 = N_2 = 10^5$ and $E_{\text{excite}} = 2000\mu B$). Ω_{12} is sharply peaked at the point where the energy is shared equally between the two systems, which means in this case that their temperature is the same. The system is overwhelmingly likely to be in one of the microstates in the immediate vicinity of this maximum, where the entropy of the combined system is maximised. Though a toy model, this basically illustrates what is going on every time two macroscopic bodies reach thermal equilibrium.

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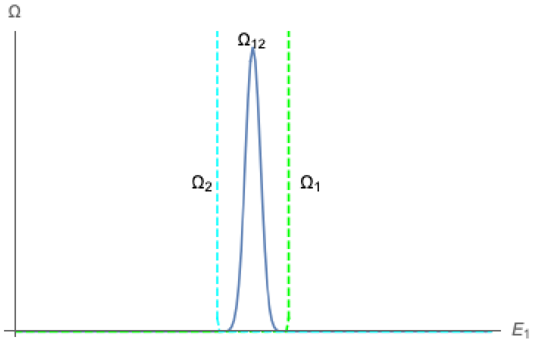
[2] This is actually slightly surprising, because it seems to imply $\Omega = 2^N$ – but that is ALL microstates. For large N, the distribution is so sharply peaked that the overwhelming majority of the microstates ARE at the peak! Including subleading terms in Stirling's approximation give $S_{\max}$ less than S_{total} by a term of order $\log N$, which allows for a peak width which is of order $\sqrt{N}$.



2.4.2 The ideal gas, first attempt

To do the ideal gas properly we need to know the quantum states of particles in a box. We learned this in PHYS20101 last semester, so we will be able to tackle it properly later. However with much less work we can at least discover how the entropy depends on volume at fixed particle number and energy.

Consider an isolated system of N atoms in a box of volume V. Imagine the box subdivided into many tiny cells of volume ΔV, so that there are $V/\Delta V$ cells in all (this number should be much greater than N). Now each atom can be in any cell, so there are $V/\Delta V$ microstates for each atom, and $(V/\Delta V)^N$ microstates for the gas as a whole. Thus

$$S = Nk_B \ln\left(\frac{V}{\Delta V}\right). \tag{2.22}$$

As a result the change in entropy when the volume changes (at fixed energy) is

$$\Delta S = Nk_B \ln\left(\frac{V_f}{V_i}\right). \tag{2.23}$$

This is exactly what we found from classical thermodynamics, A.7, and incidentally it validates the k_B in $S = k_B \ln\Omega$. From the entropy we have

$$\begin{aligned}\frac{P}{T} &= \left(\frac{\partial S}{\partial V}\right)_{E,N}\\ \Rightarrow\ P &= \frac{Nk_BT}{V}\\ \Rightarrow\ PV &= Nk_BT \qquad (2.24)\end{aligned}$$

So we have derived the ideal gas equation from first principles!

A problem with this expression for the entropy is that it depends on the size ΔV of the imaginary cells into which we subdivided our box. This is clearly unsatisfactory (though at least entropy *changes* are independent of it), but classical physics can't do any better. Quantum physics can though! If you want to jump ahead to see the full expression (called the Sackur-Tetrode equation) see here.

Chapter 3

Statistical Physics of Non-isolated Systems

Take-home message: For macroscopic systems results can be more easily obtained by regarding the temperature, rather then the energy, as fixed.

In principle, with the tools of the last section we could tackle all the problems we want now. But it turns out to be hard to calculate the entropy of any isolated system more complicated than an ideal paramagnet. This is because in an isolated system the energy is fixed, and it becomes complicated to work out all the possible ways the total energy can be split between all the atoms of the system: we can't treat each atom as independent of all the others, even if they are non-interacting.

We don't have to consider isolated systems though. In this section we will consider systems in contact with a heat bath, so that their temperature, rather than their energy, is constant. This has the advantage that if the atoms of a system don't interact with one another, they *can* be treated independently.

For a macroscopic system, there is very little difference in the results from the two approaches. If the temperature is held constant the energy will fluctuate, but the fractional size of the fluctuations decreases as $1/\sqrt{N}$ and so, from a macroscopic point of view, the energy does not appear to vary and it makes little difference whether the heat bath is there or not. So lots of results we obtain in this section are also applicable to isolated, macroscopic systems.

We will introduce something call the **partition function** from which we can calculate the energy, pressure etc. The heart of the partition function is the **Boltzmann distribution**, already met last year, which gives the probability that a particle in contact with a heat bath will have a given energy.

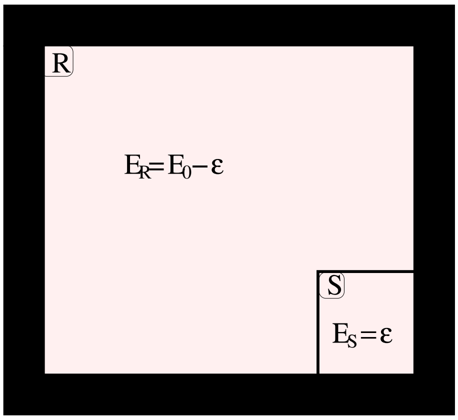
3.1 The Boltzmann Distribution

Take-home message: The form of the Boltzmann distribution!

- **Mandl** 2.5
- (**Bowley and Sánchez** 5.1)
- **Kittel and Kroemer** 3

If a system is in contact with a heat bath at temperature T, the probability that it is in the ith microstate, with energy ε_i, is given by the Boltzmann distribution.

The details of the derivation are as follows. We consider a system S in contact with a heat reservoir R, the whole forming a single isolated system with energy E_0 which is fixed but which can be differently distributed between its two parts. We can apply what we already know about isolated systems to the whole, to obtain information about the probabilities of the microstates of S,.



Heat can be exchanged between the system and reservoir, and the likelihood of a particular partition depends on the number of microstates of the whole system $S + R$ corresponding to that partition. (The equilibrium partition will be the one which maximises the number of microstates, but that is not what we are interested in here.) Since the system and reservoir are independent, the total number of microstates factorises: $\Omega = \Omega_S \Omega_R$

Now suppose we *specify* the microstate of S that we are interested in, say the ith (with energy ε_i) and ask:

- what is the probability p_i of finding the system in that microstate?

It will be proportional to the number of compatible microstates $\Omega(E_0, \varepsilon_i)$ of the whole system $S + R$. However $\Omega_S = 1$ as we've specified the state of S, so only the microstate of the reservoir is unspecified: $\Omega(E_0, \varepsilon_i) = \Omega_R(E_0 - \varepsilon_i)$

Using the relation between Ω and entropy, we can write

$$p_i \propto \Omega_R(E_0 - \varepsilon_i) = \exp\{S_R(E_0 - \varepsilon_i)/k_B\} \tag{3.1}$$

If R is to be a good reservoir, it must be much bigger than S, so $\varepsilon_i \ll E_0$. Thus we can expand S_R about $S_R(E_0)$ and keep only the lowest terms:

$$S_R(E_0 - \varepsilon_i) = S_R(E_0) - \varepsilon_i \left(\frac{\partial S_R}{\partial E}\right)_{V,N} + \tfrac{1}{2}\varepsilon_i^2 \left(\frac{\partial^2 S_R}{\partial E^2}\right)_{V,N} + \dots \tag{3.2}$$

where the derivatives are evaluated at E_0. But the derivative of S with respect to E is just the inverse of the temperature. Dropping the third term as negligibly small,[1]

$$p_i \propto \exp\{S_R(E_0)/k_B - \varepsilon_i/(k_B T)\} \propto \exp\{-\varepsilon_i/(k_B T)\} \tag{3.3}$$

---

[1] $(\frac{\partial^2 S_R}{\partial E^2})_{V,N} = \frac{\partial}{\partial E}(\frac{1}{T})_{V,N} = -\frac{1}{T^2} \times \frac{1}{C_V}$, so for $\varepsilon_i \sim k_B T \ll C_V T \sim E_0$, the second derivative contribution to (3.1) is suppressed by ε_i/E_0 which is assumed to be very much less than 1. Higher derivativees will be further suppressed.

(since $S_R(E_0)$ is a constant, independent of the microstate we are interested in). Calling the constant of proportionality $1/Z$, this is our result:

$$\boxed{p_i = \frac{e^{-\varepsilon_i/k_BT}}{Z}} \tag{3.4}$$

The normalisation constant Z is found by saying that the probability that the system is in *some* microstate is one: $\sum_j p_j = 1$, so

$$Z = \sum_j e^{-\varepsilon_j/k_BT} \tag{3.5}$$

To recap: if we specify the microstate (with a given energy) of S, the probability of this depends of the number of microstates of the reservoir with the remaining energy. This decreases with decreasing reservoir energy in just the way given by the Boltzmann distribution.

For an ideal gas or paramagnet, where interactions between atoms can be ignored, any individual particle can be considered as the system S. In that case the Boltzmann distribution holds for the state of an individual atom (hence typical first-year applications like the variation of pressure with height in the atmosphere, and the distribution of velocities of atoms in a gas).

For the spin-$\frac{1}{2}$ paramagnet in a magnetic field B there only are two energy states; $\varepsilon_\uparrow = -\mu B$ and $\varepsilon_\downarrow = \mu B$. So

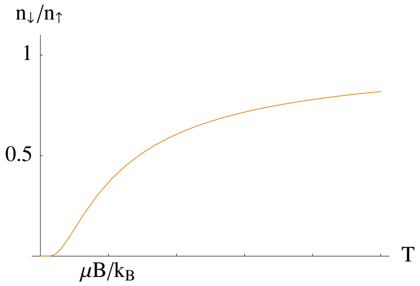
$$\begin{aligned} p_\uparrow &= \frac{e^{\mu B/k_BT}}{Z_1} \\ p_\downarrow &= \frac{e^{-\mu B/k_BT}}{Z_1} \\ \text{and} \quad Z_1 &= e^{\mu B/k_BT} + e^{-\mu B/k_BT} \end{aligned} \tag{3.6}$$

(The label on Z_1 refers to the fact that we are talking about the state of a single particle.)

In the whole system of N atoms, the number of up-spins on average will be $\langle n \rangle_\uparrow = Np_\uparrow$, so we have

$$\left\langle \frac{n_\downarrow}{n_\uparrow} \right\rangle = e^{-2\mu B/k_BT} \tag{3.7}$$

This is exactly consistent with the expression we found for the temperature of the isolated system with a fixed number of up-spins (and hence energy).



Note that in thermal equilibrium, the average number of particles in the higher energy state is *always* less than the number in the lower energy state. As the temperature tends to infinity the ratio approaches, but never exceeds, one.

3.2 The Partition Function

- **Mandl** 2.5
- **Bowley and Sánchez** 5.2
- **Kittel and Kroemer** 3

Take-home message: Far from being an uninteresting normalisation constant, Z is the key to calculating all macroscopic properties of the system!

The normalisation constant in the Boltzmann distribution is also called the partition function:

$$Z = \sum_j e^{-\varepsilon_j/k_BT} \tag{3.8}$$

where the sum is over all the microstates of the system. [2]

How can a constant be a function? Well for a given system and reservoir, that is fixed temperature, particle number, volume or magnetic field (as appropriate), Z is a constant. But if the temperature etc are allowed to vary, then Z is a function of them: $Z = Z(T, N, V)$ or $Z = Z(T, N, B)$. (The dependence on V or B comes through the energies of the microstates ε_i)

Why are we emphasising this? Because if we know Z, we can calculate all macroscopic properties of the system – energy, pressure, magnetisation, entropy…

For instance the average energy $\langle E\rangle$ (actually an ensemble average) is

$$\langle E\rangle = \sum_i \varepsilon_i\, p_i = \frac{\sum_i \varepsilon_i e^{-\varepsilon_i/k_BT}}{\sum_j e^{-\varepsilon_j/k_BT}} \tag{3.9}$$

The top line is like the bottom line (the partition function) except that each term is multiplied by ε_i. We can get the top line from the bottom by differentiating by "$1/(k_BT)$". This is a bit awkward, so we introduce a new symbol

$$\beta \equiv \frac{1}{k_BT} \tag{3.10}$$

giving

$$\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}_{N,V} \tag{3.11}$$

or

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial \beta} \tag{3.12}$$

(where—contrary to the strict instructions given earlier—we will take it for granted that it is particle number and volume or magnetic field constant that we are holding constant.)

When we calculate averages using the Boltzmann probabilities, at fixed temperature, the corresponding ensemble is called the canonical ensemble.

From the energy we can find the heat capacity:

$$C_V = \left(\frac{\partial \langle E\rangle}{\partial T}\right)_{V,N}. \tag{3.13}$$

---

[2] Recall that the microstate is of the whole system, and so the energies ϵ_i are *not* necessarily small; for a mole of gas they could be of the order kJ. It would be easy to forget this, because in a lot of the applications, like the last one, we will in fact apply it to single spins and particles with energies of the order eV or smaller.

We have found the average energy, but there will be fluctuations as heat is randomly exchanged between the system and the heat bath. These are given by

$$(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2 \tag{3.14}$$

$(\Delta E)^2$ is related to the heat capacity as follows. Since

$$\langle E^2 \rangle = \frac{1}{Z}\left(\frac{\partial^2 Z}{\partial \beta^2}\right)_{N,V} \tag{3.15}$$

(which should be obvious by analogy with the corresponding expression for $\langle E \rangle$) we obtain

$$(\Delta E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial T}{\partial \beta}\frac{\partial \langle E \rangle}{\partial T} = (k_B T)^2 \frac{C_V}{k_B} \tag{3.16}$$

For a normal macroscopic system the average energy is of the order of $N k_B T$ and the heat capacity is of the order of $N k_B$. Thus

$$\frac{\Delta E}{E} \approx \frac{1}{\sqrt{N}} \tag{3.17}$$

For a system of 10^{24} atoms, $\Delta E/E \approx 10^{-12}$ and so fluctuations are unobservable. There is no practical difference between an isolated system of energy E and one in contact with a heat bath at the same temperature.

There are exceptions. Near a critical point—where the distinction between two phases disappears—the heat capacity becomes very large and the fluctuations do too. This can be observed as "critical opalescence" where the meniscus between the liquid and gas phases disappears and the substance becomes milky and opaque and scatters light. A video and emplanation of an analogous phenomenon can be found here courtesy of

3.3 Entropy, Helmholtz Free Energy and the Partition Function

Take-home message: Once we have the Helmholtz free energy F we can calculate everything else we want.

- **Mandl** 2.5
- (**Bowley and Sánchez** 5.3-6)
- **Kittel and Kroemer** 3

We can't use an ensemble average directly for the entropy, because it doesn't make sense to talk about the entropy of a microstate. But we can talk about the entropy of the *ensemble* since the many copies can be in many different microstates. So we define the entropy of the system as the entropy of the ensemble divided by the number of copies, ν, in the ensemble: $\langle S \rangle = S_\nu/\nu$.

The ensemble has ν_i copies in the ith microstate, so the number of ways of arranging these is

$$\Omega_\nu = \frac{\nu!}{\nu_1!\,\nu_2!\,\nu_3!\ldots} \tag{3.18}$$

(compare the ways of arranging counters on the in the chequerboard).

So, using Stirling's approximation,

$$\begin{aligned}
\ln\Omega_\nu &= \nu\ln\nu - \nu - \sum_i(\nu_i\ln\nu_i - \nu_i)\\
&= \sum_i \nu_i(\ln\nu - \ln\nu_i) \qquad (\text{using } \nu = \textstyle\sum_i \nu_i \text{ in two places})\\
&= -\sum_i \nu_i(\ln\nu_i/\nu)\\
&= -\nu\sum_i p_i\ln p_i
\end{aligned} \tag{3.19}$$

So the ensemble entropy is $S_\nu = k_B\ln\Omega_\nu$ and the system entropy is

$$\boxed{\langle S\rangle = -k_B\sum_i p_i\ln p_i} \tag{3.20}$$

This expression is called the *Gibbs entropy*. (Note that as all p_i lie between 0 and 1, the entropy is positive.)

Note that we have not said anything about what distribution the probabilities p_i follow. For an isolated system, $p_i = 1/\Omega$ for each of the Ω allowed microstates, giving the Boltzmann entropy $S = k_B\ln\Omega$ as before. For a system in contact with a heat bath, p_i is given by the Boltzmann distribution, so

$$\begin{aligned}
\langle S\rangle &= -k_B\sum_i p_i\ln p_i\\
&= -k_B\sum_i p_i(-\varepsilon_i\beta - \ln Z)\\
&= k_B(\langle E\rangle\beta + \ln Z)\\
&= \frac{\langle E\rangle}{T} + k_B\ln Z
\end{aligned} \tag{3.21}$$

Rearranging we get $k_BT\ln Z = -\langle E\rangle + T\langle S\rangle = -\langle F\rangle$ where F is the Helmholtz free energy, or

$$\boxed{F = -k_BT\ln Z.} \tag{3.22}$$

Since $F = E - TS$, from the fundamental thermodynamic relation we obtain $\mathrm{d}F = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N$. Thus

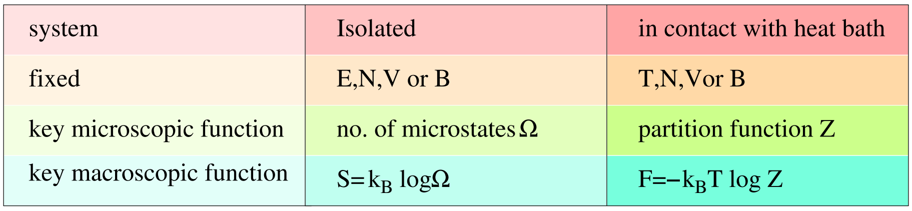
$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}} \tag{3.23}$$

(You first met these in the derivation of Maxwell's relations.) For a magnetic system, we have $m = -\left(\partial F/\partial B\right)_{T,N}$ instead of the equation for P.

Remember, Z and hence F depend on V (or B) through the energies of the microstates. For instance the energy levels of a particle in a box of side L are proportional to $\hbar^2/(mL^2) \propto V^{-2/3}$.

These relations are reminiscent of those we met in the case of an isolated system, but there the entropy was the key; here it is the Helmholtz free energy. We can make the following comparison:

It should not surprise us to find that the Helmholtz free energy is the key to a system at fixed temperature (in contrast to the entropy for an isolated system) as that is what we found classically (see here.)



system	Isolated	in contact with heat bath
fixed	E,N,V or B	T,N,Vor B
key microscopic function	no. of microstates Ω	partition function Z
key macroscopic function	$S = k_B \log\Omega$	$F = -k_B T \log Z$

3.4 The Gibbs entropy

Take-home message: The state of maximum entropy can be thought of as the one in which a determination of the microstate would cause the most information gain

We derived the expression $S = -k_B \sum_i p_i \ln p_i$ from an ensemble average, essentially using the law of large numbers and the ergodic hypothesis. We did not use any other result in statistical physics at that point, and so it is tempting to think that it tells us something about a probability distribution in a more general context.

In fact the expression was independently derived in the context of information theory by Shannon (without the k_B). The idea is that if S is large, there must be many outcomes all with non-vanishing probabilities, that is we do not know what the outcome is likely to be in advance. On the other hand if one outcome is virtually certain, $S \approx 0$. So the initial S, reflecting our prior knowledge from which we have calculated the p_i, gives us a measure of how much information we gain on average by actually finding out the outcome.

The form was derived by considering a "surprise function" $S(p)$ quantifying the information gain associated with a particular outcome of probability p. It must be positive for $0 < p \leq 1$ and satisfy $S(1) = 0$ (no surprise if the outcome is certain). Furthermore for two independent events the probability of a particular pair of outcomes with probabilities p and q is pq; but if they are independent it is reasonable that the information gained is additive: $S(pq) = S(p) + S(q)$. Only $S = -c \ln p$ has these properties. Then for a distribution, $S = -\sum_i p_i \ln p_i$ is the "average surprise" (defined up to an arbitrary multiplicative constant).[3]

Modern statistical physics starts from the Gibbs / Shannon entropy and derives the equilibrium distributions (the set of p_i), from the following principle: the equilibrium entropy should be maximised subject to constraints. For the microcanonical distribution the only constraint is that the sum of the probabilities is 1. To obtain the Boltzmann distribution the constraint is not on the temperature but the average energy, which amounts to the same thing.

How do we minimise with constraints? We use the method of Lagrange multipliers (section A.2). For a set of n constraints which are functions of the set of probabilities $u_n(p_i)$ and which are required to vanish, instead of minimising S, we minimise $S + \sum_n \lambda_n u_n$ with respect to all the p_i.

To obtain the microcanonical distribution, for which all Ω accessible microstates have the same energy, we need, for all j,

$$\frac{\mathrm{d}}{\mathrm{d}p_j}\left(-k_B \sum_i p_i \ln p_i + \lambda\Big(\sum_i p_i - 1\Big)\right) = 0 \qquad \Rightarrow -k_B\Big(\ln p_j + 1\Big) + \lambda = 0, \tag{3.24}$$

from which, rearranging, we get

$$p_j = \exp(-1 + \lambda/k_B) \tag{3.25}$$

---

[3] Shannon used logarithm to the base 2, which introduces a factor of $1/\ln 2$.

The exact form is uninformative (we don't know immediately know λ) but the principle is not: all probabilities are equal. We have derived the principle of equal a priori probabilities by maximising the Gibbs entropy. (We can then say that $p_i = 1/\Omega$ and solve for λ if we want.)

To obtain the canonical distribution, for which the microstates have different energies ϵ_i, constraining the average energy to be $\overline{E}$ we need, for all j,

$$\frac{\mathrm{d}}{\mathrm{d}p_j}\left(-k_B\sum_i p_i\ln p_i + \lambda_1\Big(\sum_i p_i - 1\Big) + \lambda_2\Big(\sum_i \epsilon_i p_i - \overline{E}\Big)\right) = 0 \tag{3.26}$$

It is left as an exercise to show that we recover the Boltzmann distribution and to identify the two Lagrange multipliers in terms of β and Z.

Finally the grand canonical distribution has microstates with variable particle number and we fix the average $\overline{N}$; we obtain the Gibbs distribution which we will meet in the next chapter, and the third Lagrange multiplier is related to the chemical potential.

In the context of information theory, the procedure of maximising S subject to the constraints is used a as way of finding an unbiased prior estimate of the probabilities. (It is not always possible to conduct infinite numbers of trials in order to assign probabilities in proportion to the frequencies!)

3.5 The paramagnet at fixed temperature

Take-home message: Understand the paramagnet and you are close to mastering the subject!

- **Mandl** 3
- (**Bowley and Sánchez** 5.7)
- (**Kittel and Kroemer** 3)

First, recap previous sections on the isolated spin-$\frac{1}{2}$ paramagnet at zero and non-zero magnetic field.

The ideal paramagnet is a lattice of N sites at each of which the spin points either up or down. Each of these has a magnetic moment $\pm\mu$. In an external field, these two states will have different energy; spin-up has energy $-\mu B$, and spin-down, μB. As we saw previously the partition function for a single atom is therefore

$$Z_1 = e^{\mu B/k_BT} + e^{-\mu B/k_BT} = 2\cosh\left(\frac{\mu B}{k_BT}\right) = 2\cosh\left(\mu B\beta\right) \tag{3.27}$$

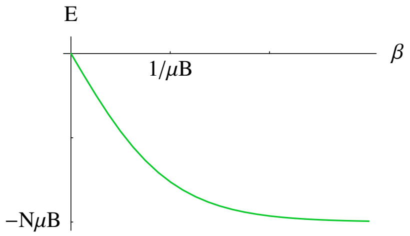
(Remember $\beta = 1/k_BT$.)

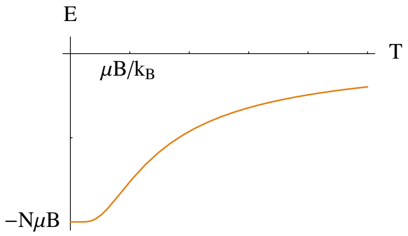
Since the atoms are non-interacting, the total energy and magnetisation of the system are just N times the average energy and magnetisation of a single spin. The energy is

$$\langle E\rangle = -N\frac{\partial \ln Z_1}{\partial\beta} = -N\mu B\tanh(\mu B\beta) \tag{3.28}$$

(For a refresher on hyperbolic trig functions, see here.)

At low T, all the spins are aligned with the field and the energy per spin is close to $-\mu B$. However as T increases, thermal fluctuations start to flip some of the spins; this is noticeable

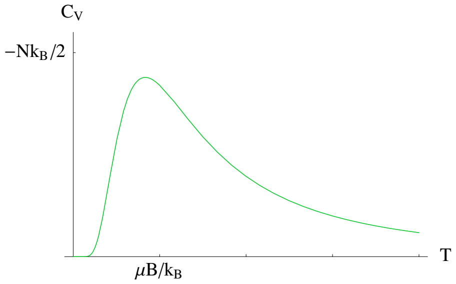




when k_BT is of the order of μB. As T gets very large, the energy tends to zero as the number of up and down spins become more nearly equal. Remember, $\langle n_\downarrow / n_\uparrow \rangle = \exp(-2\mu B/k_BT)$, so it never exceeds one.

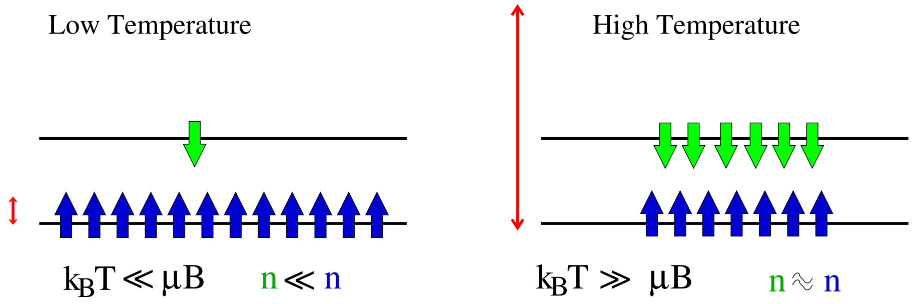
We can also calculate the heat capacity :

$$C_V = \frac{\partial E}{\partial T} = N k_B \, (\mu B \beta)^2 \, \mathrm{sech}^{\,2}(\mu B \beta) \tag{3.29}$$



We see that the heat capacity tends to zero both at high and low T. At low T the heat capacity is small because k_BT is much smaller than the energy gap $2\mu B$, so thermal fluctuations which flip spins are rare and it is hard for the system to absorb heat. This behaviour is universal; quantisation means that there is always a minimum excitation energy of a system and if the temperature is low enough, the system can no longer absorb heat.

The high-T behaviour arises because the number of down-spins never exceeds the number of up-spins, and the energy has a maximum of zero. As the temperature gets very high, that limit is close to being reached, and raising the temperature still further makes very little difference. This behaviour is *not* universal, but only occurs where there is a finite number of energy levels (here, there are only two). Most systems have an infinite tower of energy levels, there is no maximum energy and the heat capacity does not fall off.



Up to now we've cheated a bit, (though the results are correct,) in that we didn't calculate the partition function for the whole system, only for a single spin. It is easy to show however that the partition function for N non-interacting spins on a lattice is

$$Z_N = (Z_1)^N \tag{3.30}$$

Let's start with a system that has two single-particle energy levels, ε_1 and ε_2. The single-particle partition function is

$$Z_1 = e^{-\varepsilon_1 \beta} + e^{-\varepsilon_2 \beta}. \tag{3.31}$$

The partition function for two distinguishable particles is

$$Z_2 = e^{-2\varepsilon_1 \beta} + 2e^{-(\varepsilon_1+\varepsilon_2)\beta} + e^{-2\varepsilon_2 \beta} = (Z_1)^2, \tag{3.32}$$

where the second state is multiplied by 2 because there are two ways that two *distinguishable* particles can be in different levels.

In general, for N particles, the energies are $n\varepsilon_1 + (N-n)\varepsilon_2$, for $0 \le n \le N$, and there are $N!/n!(N-n)!$ separate microstate of this energy. So

$$\begin{aligned}
Z_N &= \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} \mathrm{e}^{-(n\varepsilon_1+(N-n)\varepsilon_2)\beta} \\
&= \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} \mathrm{e}^{-n\varepsilon_1\beta} \mathrm{e}^{-(N-n)\varepsilon_2\beta} \\
&= \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} \left(\mathrm{e}^{-\varepsilon_1\beta}\right)^n \left(\mathrm{e}^{-\varepsilon_2\beta}\right)^{N-n} = (Z_1)^N
\end{aligned} \tag{3.33}$$

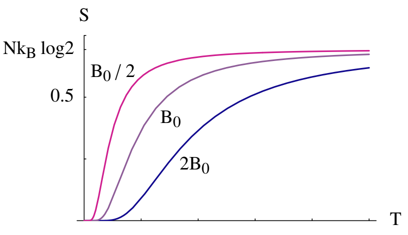
where we've used the binomial expansion of $(x+y)^N$.

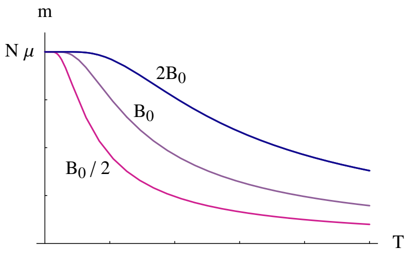
If there are more than two energy levels, Z_1 has more terms, but a similar derivation can be done. However we won't show it because it is just a special case of a future section.

Since $\langle E_N \rangle$ is derived from $\ln Z_N$, we see immediately that the results for N particles will just be N times the single particle values, as we assumed at the start of this section. We can also calculate the Helmholtz free energy, $F = -k_B T \ln Z_N$. The magnetisation, $m = -(\partial F/\partial B)_{T,N}$, gives $m = -E/B$ as expected. We can find the entropy, from $S = -(\partial F/\partial T)_{B,N}$ or from $S = (E-F)/T$:

$$\langle S \rangle = N k_B \Big(\ln\left(2\cosh(\mu B \beta)\right) - \mu B \beta \tanh(\mu B \beta) \Big) \tag{3.34}$$

Below we plot S and m against temperature for several different external fields. At zero temperature, the magnetisation goes to $N\mu$: all the spins are up. There is no disorder, and so the entropy is zero.





The stronger the field, the higher the temperature has to be before the spins start to be appreciably disordered.

At high temperatures the spins are nearly as likely to be up as down; the magnetisation falls to zero and the entropy reaches a maximum. The entropy of this state is $Nk_B \ln 2$, as we have already seen.

There is a caveat to the formula $Z_N = (Z_1)^N$. The argument says that there are a number of different microstates with the same number of up and down spins. Since the spins are arranged on a lattice, this is correct; every spin can be distinguished from every other spin by its position. When we go on to consider a gas, however, this is no longer so, and the relation between Z_1 and Z_N changes. The treatment for indistinguishable particles is here.

Returning to the expression for the partition function for two distinguishable two-state particles, (3.32), we see that two microstates have the same energy $\varepsilon_1 + \varepsilon_2$ and instead of listing them twice we have written it once and multiplied by two. We say that this energy is "doubly degenerate" or has a **degeneracy** of two. In general we can write the partition function as as sum over distinct energies ε_n rather than over all microstates if we include the degeneracies g_n:

$$Z = \sum_j e^{-\varepsilon_j \beta} = \sum_n g_n e^{-\varepsilon_n \beta}.$$

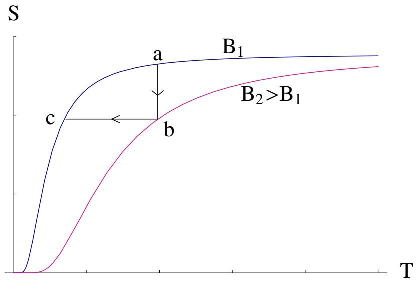
The first sum runs over microstates, the second over energies.

3.6 Adiabatic demagnetisation and the third law of thermodynamics

Take-home message: The properties of a paramagnet can be put to practical use to achieve low temperatures, but we can never get to absolute zero.

- **Mandl** 5.6

By magnetising and demagnetising a paramagnetic sample while controlling the heat flow, we can lower its temperature.



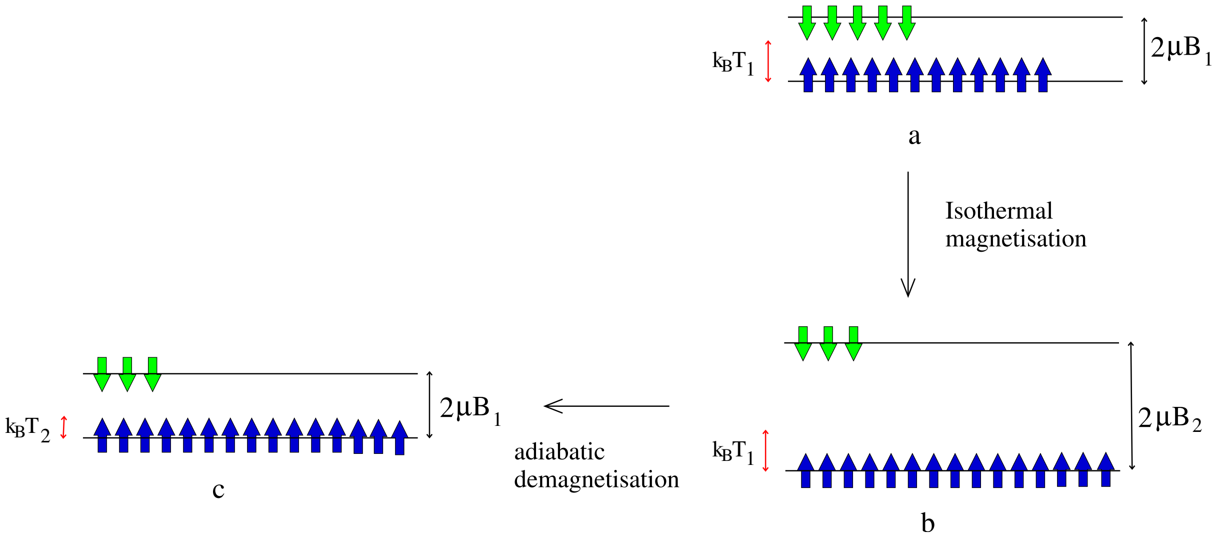
We start with the sample in a magnetic field B_1 at an (already fairly low) temperature T_1.

a→ b: With the sample in contact with a heat bath at T_1, we increase the magnetic field to B_2.

b→ c: With the sample now isolated, we slowly decrease the field to B_1 again. This is the adiabatic demagnetisation step; because the process is slow and adiabatic, the entropy is unchanged.

By following these steps on a $T-S$ plot, we see that the second, constant entropy, step, reduces the temperature. The entropy is a function of B/T only, not B or T separately (see here) so if we reduce B at constant S, we reduce T also.

The following figure shows what is happening to the spins. In the first step we increase the level spacing while keeping the temperature constant, so the population of the upper level falls. In the second step we reduce the level spacing again, but as the spins are isolated there is no change in level occupation. The new, lower level occupation is now characteristic of a lower temperature than the original one.



If we start with a large sample, we could repeat the process with a small sub-sample, the remaining material acting as a heat bath during the next magnetisation. By this method temperatures of a fraction of a Kelvin can be reached. However after a few steps less and less is gained each time, as the curves come together as $T \to 0$. (Once the electron spins are all ordered, one can start to order the nuclear spins, and reach even lower temperatures—the magnetic moment of the nucleus is around a two-thousandth of that of the atom), but even that has its limits.

This is an important and general result. There is always a minimum excitation energy ε of the system, and once $k_BT \ll \varepsilon$ there is no further way of lowering the temperature. The unattainability of absolute zero is the **third law of thermodynamics**.

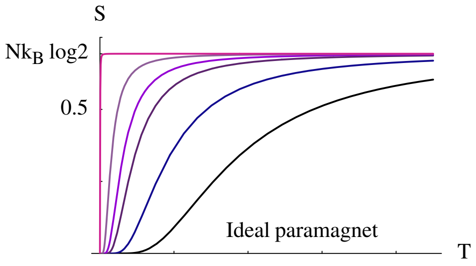
The laws of Thermodynamics

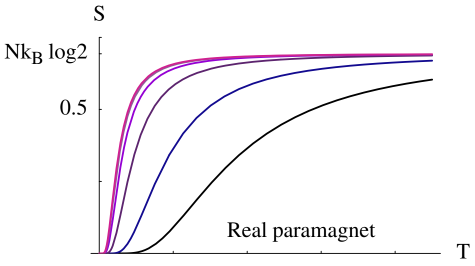
1: You can't win, you can only break even.

2: You can only break even at T=0.

3: You can't reach T=0....

In the process above, the lowest temperature attainable is obviously proportional to $\mu B_1/k_B$. You might wonder why we can't just take $B_1 \to 0$. But in any real paramagnet, there is a weak coupling between the spins which means that they prefer to be aligned with one another. If we remove the external field, this coupling acts like a weak internal field, and at low enough temperatures the spins will still be ordered. The strength of this coupling is then what governs the lowest attainable temperature.





3.7 Vibrational and rotational energy of a diatomic molecule

Take-home message: Along with the next section, the partition function allows us to predict the temperature-dependent internal energy and heat capacities of diatomic gases, based on quantum mechanics

- (**Bowley and Sánchez** 5.11,5.12)

So far we have only looked at two-level systems such as the paramagnet. More usually there are many or even infinitely many levels, and hence terms in the partition function. In some special cases the partition function can still be expressed in closed form.

Vibrational energy of a diatomic molecule

The energy levels of a quantum simple harmonic oscillator of frequency ω are

$$\varepsilon_n = (n + \tfrac{1}{2})\hbar\omega \qquad n = 0, 1, 2 \ldots \tag{3.35}$$

so

$$\begin{aligned} Z_1 &= \sum_{n=0}^{\infty} e^{-\varepsilon_n \beta} = e^{-\frac{1}{2}\hbar\omega\beta}\left(e^0 + e^{-\hbar\omega\beta} + e^{-2\hbar\omega\beta} \ldots\right) \\ &= \frac{e^{-\frac{1}{2}\hbar\omega\beta}}{1 - e^{-\hbar\omega\beta}} \\ &= \Big(2\sinh(\tfrac{1}{2}\hbar\omega\beta)\Big)^{-1} \end{aligned} \tag{3.36}$$

where we have used the expression for the sum of a geometric series, $\sum_n x^n = (1-x)^{-1}$, with $x = e^{-\hbar\omega\beta}$.

From this we obtain

$$\langle E_1 \rangle = -\frac{\partial \ln Z_1}{\partial \beta} = \tfrac{1}{2}\hbar\omega \coth\left(\tfrac{1}{2}\hbar\omega\beta\right). \tag{3.37}$$

The low temperature limit of this ($k_B T \ll \hbar\omega$; $\hbar\omega\beta \to \infty$) is $\frac{1}{2}\hbar\omega$, which is what we expect if only the ground state is populated. The high temperature limit ($k_B T \gg \hbar\omega$; $\hbar\omega\beta \to 0$) is $k_B T$, which should ring bells! (See here for more on limits.)

Typically the high temperature limit is only reached around 1000 K.

Rotational energy of a diatomic molecule
The energy levels of a rigid rotor of moment of inertia $\mathcal{I}$ are

$$\varepsilon_l = \frac{l(l+1)\hbar^2}{2\mathcal{I}} \qquad l = 0, 1, 2\ldots \tag{3.38}$$

but there is a complication; as well as the quantum number L there is m_l, $-l \le m_l \le l$, and the energy doesn't depend on m_l. Thus the lth energy level occurs $2l+1$ times in the partition function, giving

$$Z_1 = \sum_{l=0}^{\infty} \sum_{m_l=-l}^{l} e^{-l(l+1)\hbar^2\beta/2\mathcal{I}} = \sum_{l=0}^{\infty} (2l+1)\, e^{-l(l+1)\hbar^2\beta/2\mathcal{I}}. \tag{3.39}$$

The term $2l+1$ is called a **degeneracy factor** since "degenerate" levels are levels with the same energy. (I can't explain this bizarre usage, but it is standard.) For general β this cannot be further simplified. At low temperatures successive term in Z_1 will fall off quickly; only the lowest levels will have any significant occupation probability and the average energy will tend to zero.

At high temperatures, ($k_BT \gg \hbar^2/2\mathcal{I}$) there are many accessible levels and the fact that they are discrete rather than continuous is unimportant; we can replace the sum over l with an integral dl; changing variables to $x = l(l+1)$ gives

$$\begin{aligned} Z_1 &= \frac{2\mathcal{I}}{\hbar^2\beta} \\ \langle E_1 \rangle &= k_BT \end{aligned} \tag{3.40}$$

Typically $\hbar^2/2\mathcal{I}$ is around 10^{-3} eV, so the high-temperature limit is reached well below room temperature.

It is not an accident that the high-temperature limit of the energy was k_BT in both cases! These are examples of **equipartition** which is the subject of a future section.

3.8 Translational energy of a molecule in an ideal gas

Take-home message: We can calculated the translational energy too. We are not done with the idea gas though....

- **Mandl** 7.1-4, Appendix B
- **Bowley and Sánchez** 5.9,7.2
- **Kittel and Kroemer** 3

This example is rather more complicated than the preceding ones, but the result is simple and powerful.

The non-interacting atoms of the gas are in a cuboidal box of side lengths L_x, L_y and L_z, and volume $V \equiv L_xL_yL_z$. The sides of the box are impenetrable, so the wave function ψ must vanish there, but inside the box the atom is free and so ψ satisfies the free Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z). \tag{3.41}$$

The equation, and the boundary conditions, are satisfied by

$$\psi(x,y,z) = A\sin\left(\frac{n_x\pi x}{L_x}\right)\sin\left(\frac{n_y\pi y}{L_y}\right)\sin\left(\frac{n_z\pi z}{L_z}\right) \tag{3.42}$$

with n_x, n_y and n_z integers greater than zero. The corresponding energy is

$$\varepsilon(n_x,n_y,n_z) = \left(\left(\frac{n_x\pi}{L_x}\right)^2 + \left(\frac{n_y\pi}{L_y}\right)^2 + \left(\frac{n_z\pi}{L_z}\right)^2\right)\frac{\hbar^2}{2m} \equiv \frac{k^2\hbar^2}{2m} \tag{3.43}$$

where $k^2 = k_x^2 + k_y^2 + k_z^2$ and $k_x = \pi n_x/L_x$ etc. So the one-particle partition function is

$$Z_1 = \sum_{\{n_x,n_y,n_z\}} e^{-\varepsilon(n_x,n_y,n_z)\beta}. \tag{3.44}$$

In general this cannot be further simplified. However there can be simplifications if k_BT is much greater than the spacing between the energy levels, as we saw in the rotational case. For a volume of 1 litre, that spacing is of order $\hbar^2\pi^2/2mL^2 \approx 10^{-20}$ eV—truly tiny. Even at the lowest temperatures ever reached, we are in the high-temperature regime! Thus we can replace the sum over levels by an integral. (This is called the *continuum approximation*. We choose k_x, k_y and k_z as the variables, and replace $\sum_{n_x}$ with $(L_x/\pi)\int \mathrm{d}k_x$, giving

$$\begin{aligned}
Z_1 &= \frac{L_xL_yL_z}{\pi^3}\int_0^\infty\!\!\int_0^\infty\!\!\int_0^\infty \mathrm{d}k_x\mathrm{d}k_y\mathrm{d}k_z\, e^{-\varepsilon(k)\beta} \\
&= \frac{V}{\pi^3}\int_0^\infty\!\!\int_0^{\pi/2}\!\!\int_0^{\pi/2} k^2\sin\theta_k\mathrm{d}k\,\mathrm{d}\theta_k\mathrm{d}\phi_k\, e^{-\varepsilon(k)\beta} \qquad \text{converting to spherical polar coordinates} \\
&= \frac{1}{8}4\pi\frac{V}{\pi^3}\int_0^\infty k^2\mathrm{d}k\, e^{-\varepsilon(k)\beta} \\
&\equiv \int_0^\infty g(k)e^{-\varepsilon(k)\beta}\mathrm{d}k \qquad \text{where } g(k) \equiv Vk^2/2\pi^2
\end{aligned} \tag{3.45}$$

The factor of 1/8 in the penultimate line comes from the fact that we only integrated over positive values of k_x etc, that is over the positive octant of k-space. $g(k)$ is called the **density of states** in k-space; $g(k)\mathrm{d}k$ is the number of states within range of $k \to k + \mathrm{d}k$. See here for more on this concept.

This section only depended on the fact that the energy is independent of the direction of k. Now we use the actual form of $\varepsilon(k)$ to complete the calculation:

$$\begin{aligned}
Z_1 &= \frac{V}{2\pi^2}\int_0^\infty k^2\, e^{-\hbar^2k^2\beta/2m}\mathrm{d}k \\
&= V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} \equiv Vn_Q.
\end{aligned} \tag{3.46}$$

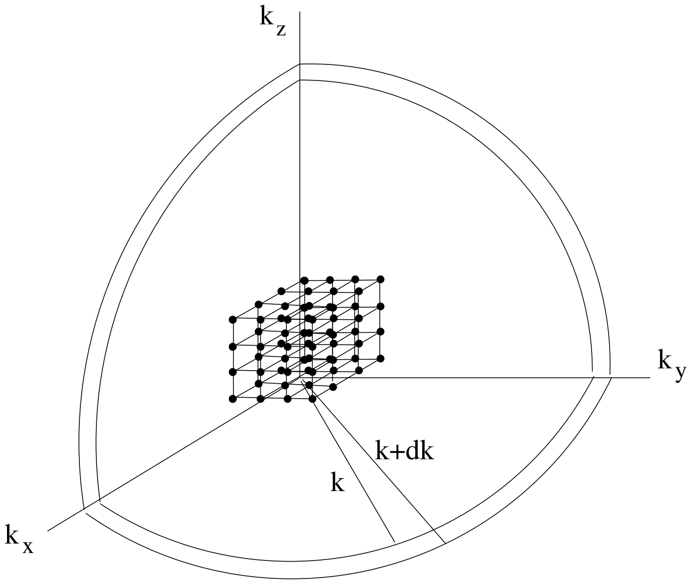
Z_1 is a pure number, so "n_Q" must have dimensions of $1/V$ like a number density; it is called the **quantum concentration** and is temperature-dependent. From Z_1 we can obtain the average single particle energy:

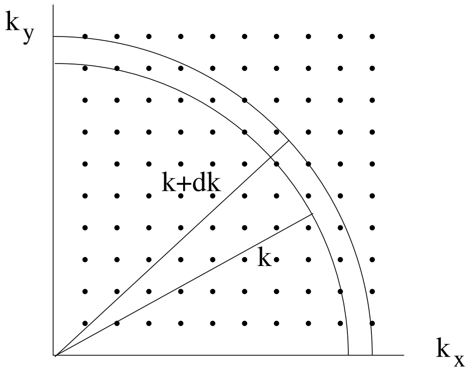
$$\langle E_1 \rangle = -\frac{\partial \ln Z_1}{\partial \beta} = \frac{3}{2} k_B T \tag{3.47}$$

as we should have expected.

3.8.1 The Density of States

Take-home message: This way of presenting the calculation for the ideal gas makes the partition function as a sum over states more intuitive.





Going through the algebra to calculate the translational partition function we turned a sum over the integers n_x, n_y and n_z which count the number of half wavelengths along the three sides, to an integral over $\mathbf{k}$. Since the energy depends only on $k = |\mathbf{k}|$, we could do the integral over the direction of $\mathbf{k}$ leaving only the integral over k; in this process we collected a number of factors and called them the **density of state**: $g(k) = Vk^2/2\pi^2$, so that

$$Z_1 = \int_0^\infty g(k)\, e^{-\varepsilon(k)\beta} \mathrm{d}k \tag{3.48}$$

We see that $g(k)$ is acting as a "degeneracy factor", which we first met in the context of the rotor. If there is more than one energy level with the same energy, and we replace the sum over individual states with a sum over allowed energies, we need to include a factor in front of the Boltzmann factor for degenerate levels so that they are counted often enough.

The picture above shows a graphical representation of the allowed states in k-space. Since

$$\mathbf{k} = \left(\frac{\pi n_x}{L_x}, \frac{\pi n_y}{L_y}, \frac{\pi n_z}{L_z} \right), \tag{3.49}$$

with n_x etc positive, the allowed values of k form a three-dimensional lattice. The density of states is the number of states within an infinitesimal range of k, and hence of energy. This is just the volume of an octant of a spherical shell, $(1/8) \times 4\pi k^2 \times \mathrm{d}k$, divided by the volume of k-space per state, π^3/V, giving

$$g(k)\mathrm{d}k = \frac{Vk^2}{2\pi^2}\mathrm{d}k. \tag{3.50}$$

We will meet this expression many times in the rest of the course. Later, we will apply it to systems of particles with spin s, where the full description of every single particle state includes the spin projection m_s, where m_s takes on $2s+1$ values at integer steps between $-s$ and s. So for a spin-$\frac{1}{2}$ particle, $m_s = -\frac{1}{2}$ or $\frac{1}{2}$; for spin-1, $m_s = -1, 0$ or 1. In these cases the spatial states specified by (3.42) corresponds to $2s+1$ distinct quantum states (all of the same energy in the absence of a magnetic field) and so the density of states has an extra degeneracy factor $g_s \equiv 2s+1$:

$$\boxed{g(k) = \frac{g_s V k^2}{2\pi^2}.} \tag{3.51}$$

and

$$\boxed{Z_1 = g_s V \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} \equiv V g_s n_Q.} \tag{3.52}$$

If expressions are given without the g_s, they apply to spin-zero particles only. It can be restored by $n_Q \to g_s n_Q$ in any expression missing it.

Later on we will also use $g(\varepsilon)$, where $\varepsilon(k)$ is the energy of a particle with momentum $\hbar k$. $g(\varepsilon)$ is defined so that the number of states with wave numbers between k and $k + \mathrm{d}k$ has to be the same as the number with energies between $\varepsilon(k)$ and $\varepsilon(k+\mathrm{d}k) = \varepsilon(k) + \mathrm{d}\varepsilon$, i.e.

$$g(k)\mathrm{d}k = g(\varepsilon)\mathrm{d}\varepsilon \qquad \text{where} \quad \mathrm{d}\varepsilon = \frac{\mathrm{d}\varepsilon}{\mathrm{d}k}\mathrm{d}k$$

So in 3D, for non-relativistic particles with $\varepsilon = \hbar^2 k^2/2m$,

$$g(\varepsilon) = \frac{g_s V (2m)^{3/2}}{4\pi^2\hbar^3}\varepsilon^{1/2}.$$

Finally, a comment on notation: Mandl uses $D(k)$ rather than $g(k)$, as I did in the notes for Thermal and Statistical Physics. Dr Galla used both! Strictly, $g(k)$ is not a degeneracy but a degeneracy density so a stricter notation would be something like $\mathrm{d}g/\mathrm{d}k$. That is what $D(k)$ is trying to indicate. The lecturers of PHYS30151, whose past exams you will be looking at in due course, used $\mathrm{d}n/\mathrm{d}k$. But the symbol n is overworked in this course as it is! Warning: Dr Xian in PHYS20252 uses $g(\varepsilon)$ to mean a double density, the number of states per unit energy and per unit (physical) volume. Hence in his notation there is no V in the density of states.

3.8.2 The Maxwell-Boltzmann Distribution

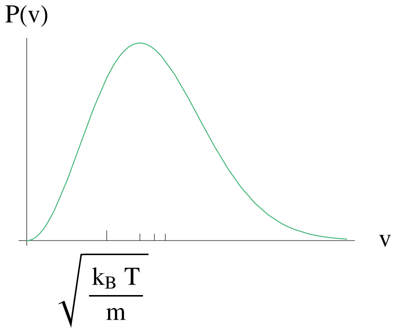
Take-home message: The density of states can be used to derive the Maxwell-Boltzmann distribution of molecular speeds in a gas.

- **Mandl** 7.7
- **Bowley and Sánchez** 7.4
- **Kittel and Kroemer** 14

The speed v of a particle is related to the wave number k by $mv = \hbar k$. We already know the probability of a particle having k in the range $k \to k+\mathrm{d}k$, and so we can immediately write down the corresponding probability of the speed being in the range $v \to \mathrm{d}v$:

$$\begin{aligned}
P(k \to k + \mathrm{d}k) &= \frac{g(k)\, e^{-\varepsilon(k)\beta}}{Z_1} \mathrm{d}k \qquad \text{where } \varepsilon(k) = \hbar^2 k^2/2m \\
P(v \to v + \mathrm{d}v) &= \frac{V}{2\pi^2} \frac{e^{-\varepsilon(v)\beta}}{Z_1} \left(\frac{m}{\hbar}\right)^3 v^2 \mathrm{d}v \qquad \text{where } \varepsilon(v) = mv^2/2 \\
\Rightarrow P(v) &= \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T} \qquad (3.53)
\end{aligned}$$

This is called the Maxwell-Boltzmann distribution, and it is plotted below.



We can find the most probable speed (from $\mathrm{d}P(v)/\mathrm{d}v = 0$), as well as the mean speed and the rms speed:

$$\begin{aligned}
v_p &= \sqrt{\frac{2k_B T}{m}} \approx 1.41 \sqrt{\frac{k_B T}{m}} \\
\langle v \rangle &= \sqrt{\frac{8k_B T}{\pi\, m}} \approx 1.60 \sqrt{\frac{k_B T}{m}} \\
v_{\mathrm{rms}} &= \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} \approx 1.73 \sqrt{\frac{k_B T}{m}} \qquad (3.54)
\end{aligned}$$

These are marked on the graph above.

Note that $\hbar$ has disappeared from $P(v)$, which can be derived from the Boltzmann distribution in a purely classical theory provided the normalisation is obtained from requiring the integral of $P(v)$ to be one.

3.9 Factorisation of partition functions

Take-home message: Where degrees of freedom are independent, the full partition function is a product of individual partition functions.

In lectures, we repeatedly use $Z_N = (Z_1)^N$ for independent distinguishable particles, and we also used $Z_1 = Z_1^{\mathrm{tr}} Z_1^{\mathrm{rot}} Z_1^{\mathrm{vib}}$ for the independent contributions of vibrational, rotation and translational degrees of freedom to a single-particle's partition function. In these notes we prove that where the energy of a system separates into independent contributions like this, the partition function factorises.

In full generality, let us suppose that a microstate has N independent contributions to its energy, the allowed values of the first being $\varepsilon_1^{(1)}$, $\varepsilon_2^{(1)}$, $\varepsilon_3^{(1)}, \ldots$, and similarly for the others, with $\varepsilon_i^{(n)}$ being the ith allowed value of the nth contribution. Also, let $Z^{(n)}$ be the partition function for the nth contribution:

$$Z^{(n)} = \sum_i \exp\left(-\varepsilon_i^{(n)}\beta\right). \tag{3.55}$$

Then the full partition function is

$$\begin{aligned}
Z &= \sum_{i,j,k,\ldots p} \exp\left(-(\varepsilon_i^{(1)} + \varepsilon_j^{(2)} + \varepsilon_k^{(3)} + \ldots + \varepsilon_p^{(N)})\beta\right) \\
&= \sum_{i,j,k,\ldots p} \exp\left(-\varepsilon_i^{(1)}\beta\right) \exp\left(-\varepsilon_j^{(2)}\beta\right) \exp\left(-\varepsilon_k^{(3)}\beta\right) \ldots \exp\left(-\varepsilon_p^{(N)}\beta\right) \\
&= \left(\sum_i \exp\left(-\varepsilon_i^{(1)}\beta\right)\right) \left(\sum_j \exp\left(-\varepsilon_j^{(2)}\beta\right)\right) \left(\sum_k \exp\left(-\varepsilon_k^{(3)}\beta\right)\right) \ldots \left(\sum_p \exp\left(-\varepsilon_p^{(N)}\beta\right)\right) \\
&= Z^{(1)} Z^{(2)} Z^{(3)} \ldots Z^{(N)}.
\end{aligned} \tag{3.56}$$

It is the step between the second and third lines, in which we interchange the order of addition and multiplication, that is tricky at first! But it is no harder than the following (in reverse):

$$(a+b+c)(p+q+r)(x+y+z) = apx+apy+apz+aqx+aqy+aqz+arx+ary+arz+bpx+\ldots+crz \tag{3.57}$$

More compactly,

$$\begin{aligned}
Z &= \sum_{i_1,i_2,\ldots i_N} \exp\left(-\sum_{n=1}^{N} \varepsilon_{i_n}^{(n)}\beta\right) \\
&= \sum_{i_1,i_2,\ldots i_N} \prod_{n=1}^{N} \exp\left(-\varepsilon_{i_n}^{(n)}\beta\right) \\
&= \prod_{n=1}^{N} \sum_{i_n} \exp\left(-\varepsilon_{i_n}^{(n)}\beta\right) = \prod_{n=1}^{N} Z^{(n)}.
\end{aligned} \tag{3.58}$$

3.10 The Equipartition Theorem

Take-home message: The classical theory of equipartition holds in the high-temperature limit

- **Mandl** 7.9
- **Bowley and Sánchez** 5.14
- (**Kittel and Kroemer** 3)

The results for vibrational, rotational and translational energies demonstrate that, at high enough temperatures, the **law of equipartition of energy** holds: each quadratic term in the classical expression for the energy contributes $\frac{1}{2}k_BT$ to the average energy and $\frac{1}{2}k_B$ to the heat capacity. The oscillator has quadratic kinetic and potential terms:

$$E_{\text{vib}} = \tfrac{1}{2}m\dot{x}^2 + \tfrac{1}{2}m\omega^2x^2 \qquad 2 \text{ d.o.f, } E \to k_BT. \tag{3.59}$$

The rotor has two perpendicular axes about which it can rotate; each with a quadratic kinetic energy (rotations about the axis have no effect in quantum mechanics; classically the moment of inertia is tiny):

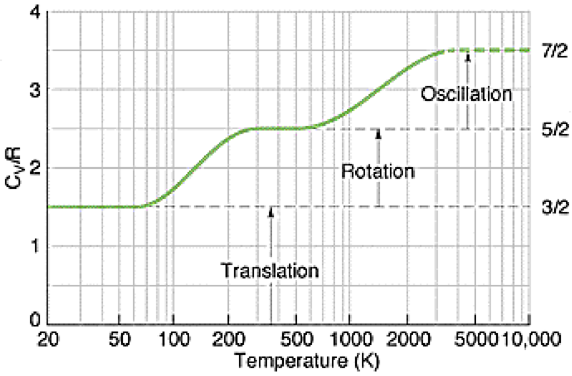
$$E_{\rm rot} = \tfrac{1}{2}\mathcal{I}\omega_1^2 + \tfrac{1}{2}\mathcal{I}\omega_2^2 \qquad 2 \text{ d.o.f, } E \to k_B T. \tag{3.60}$$

The translational kinetic energy has three terms for the three dimensions of space:

$$E_{\rm tr} = \tfrac{1}{2}m\dot{x}^2 + \tfrac{1}{2}m\dot{y}^2 + \tfrac{1}{2}m\dot{z}^2 \qquad 3 \text{ d.o.f, } E \to \tfrac{3}{2}k_B T. \tag{3.61}$$

Now we understand what governs "high enough": $k_B T$ has to be much greater than the spacing between the quantum energy levels. If this is not satisfied, the heat capacity will be reduced, dropping to zero at low temperatures. The corresponding degree of freedom is said to be **frozen out**; this is the situation for the vibrational degrees of freedom at room temperature.

Here is an idealised graph of the heat capacity of hydrogen with temperature, (©P. Eyland, University of New South Wales)



As the moment of inertia for H_2 is small, the temperature by which equipartition holds for rotational modes is actually quite high. Bowley and Sánchez have a graph taken from data (Fig. 5.8).

We can predict the specific heat of other substances based on equipartition, simply by counting the degrees of freedom. For a solid, we expect the molar heat capacity to be $3RT$ since each atom is free to vibrate in three directions. This is the law of Dulong and Petit, and it works well for a variety of solids at room temperature. (More details here.)

Equipartition does not hold, even at high temperatures, if the energy is not quadratic. For instance the gravitational potential energy is linear in height, and the average potential energy of a molecule in an isothermal atmosphere is $k_B T$, not $\frac{1}{2}k_B T$.

Similarly the kinetic energy of a highly relativistic particle is given by the non-quadratic $c\sqrt{p_x^2 + p_y^2 + p_z^2}\ (= \hbar c k)$, not by the quadratic $(p_x^2 + p_y^2 + p_z^2)/2m$, and the average kinetic energy is $3k_B T$, not $\frac{3}{2}k_B T$.

3.10.1 The heat capacity of a crystal

Take-home message: The Einstein model of independent oscillators only works quantitatively in the high-temperature limit

Based on equipartition, we expect the molar heat capacity for a solid to be $3RT$ since each atom is free to vibrate in three directions. This is the law of Dulong and Petit, and it works well for a variety of solids at room temperature. It is reproduced, as might be expected, by the

Einstein model for a crystal which considers each atom linked to its neighbours by six springs ($3N$ in total)—the algebra is just like that of the vibrations of a diatomic molecule giving

$$\begin{aligned}\langle E\rangle &= \tfrac{3}{2}N\hbar\omega\coth\left(\tfrac{1}{2}\hbar\omega\beta\right)\\ C_V &= \tfrac{3}{4}Nk_B(\hbar\omega\beta)^2\left(\sinh\tfrac{1}{2}\hbar\omega\beta\right)^{-2}\end{aligned}\tag{3.62}$$

At low temperature ($\beta \to \infty$) the energy tends to $3Nk_B(\hbar\omega\beta)^2 e^{-\hbar\omega\beta}$. Although this tends to zero, it does not agree with the observed low temperature behaviour, which is proportional to T^3. More sophisticated models, such as that of Debye, allow for collective vibrations of many atoms which have much lower frequency, and hence contribute to the internal energy and heat capacity at much lower temperatures. We will revisit this when we consider gases of bosons, not that the connection is obvious right now.

3.11 The N particle partition function for indistinguishable particles

Take-home message: atoms are fundamentally indistinguishable, and this has measurable macroscopic consequences

In the previous section we assumed that the average energy of N non-interacting atoms was the same as N times the average energy of one atom, an obvious (and correct) consequence of the law of large numbers and indeed almost the definition of "non-interacting". It could also be derived from $Z_N = (Z_1)^N$. To continue our study of the ideal gas, we want to calculate F, and from that the pressure and entropy. But recalling that

$$Z_1 = Vg_s\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} \equiv Vg_sn_Q. \tag{3.63}$$

and using $F = -k_BT\ln Z_N$ would give

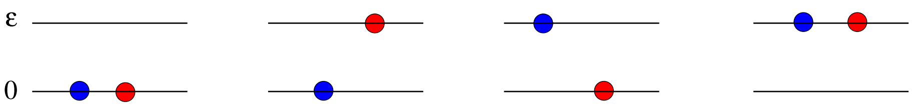
$$F = -Nk_BT\ln(Vg_sn_Q) \qquad \text{warning, incorrect!} \tag{3.64}$$

and that doesn't make sense. If one has double the number of particles, in double the volume, the Helmholtz free energy, like the energy, should double. They are both extensive variables. But the expression above is not extensive.

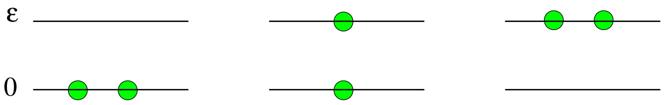
The solution comes from a very surprising quarter—quantum mechanics. Quantum mechanics says that atoms of the same element are fundamentally *indistinguishable*, exactly the same. As a result, for instance, all observables have to be unchanged when we interchange two identical atoms. We can't give them labels and know which one is in which state. But if we recall the derivation of derivation of $Z_N = (Z_1)^N$ which held for the paramagnet, crucially all N particles were distinguishable (by their position in the lattice). This is not the case for a gas. So what is the N-particle partition function for indistinguishable particles?

Consider first the partition function for the simplest case, of two particles and two energy levels. If the particles are distinguishable, as in the upper picture below, there are four states, two of which have energy ε, and the two-particle partition function is

$$Z_2 = e^0 + 2e^{-\varepsilon\beta} + e^{-2\varepsilon\beta} = (Z_1)^2 \tag{3.65}$$



Distinguishable particles



Indistinguishable particles

However for *indistinguishable* atoms, we can't give them labels and know which one is in which state. Thus there are only three states, as in the lower picture, and the partition function is

$$Z_2 = e^0 + e^{-\varepsilon\beta} + e^{-2\varepsilon\beta} \neq (Z_1)^2 \tag{3.66}$$

If we use $(Z_1)^2$, we over-count the state in which the particles are in different energy levels. In general there is no simple expression for the N-particle partition function for indistinguishable particles.

However we note that $(Z_1)^N$ over-counts the states in which all N particles are in *different* energy levels by exactly $N!$. So if we are in a position where there are many more accessible energy levels (that is, levels with energy less than a few k_BT) than there are particles, the probability of any two particles being in the same energy level is small, and almost all states will have all the particles in different levels. Hence a good approximation is

$$Z_N = \frac{(Z_1)^N}{N!} \tag{3.67}$$

It turns out that this is exactly what we need to fix the ideal gas.

3.12 The ideal gas

Take-home message: We can now derive the equation of state and other properties of the ideal gas.

- **Mandl** 7.1,7.4-6
- **Bowley and Sánchez** 6.5
- **Kittel and Kroemer** 3

We are now reaching the most important test of statistical physics: the ideal gas. For the moment we assume it is monatomic; the extra work for a diatomic gas is minimal.

The one-particle translational partition function, at any attainable temperature, is

$$Z_1 = V g_s n_Q, \qquad \text{where } n_Q \equiv \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}. \tag{3.68}$$

We already saw that assuming the atoms to be distinguishable yields a non-extensive Helmholtz free energy, and argued that we had to treat them as indistinguishable. So we want to see if we use the approximate form from the previous section,

$$Z_N = \frac{(Z_1)^N}{N!}. \tag{3.69}$$

We can, if we can convince ourselves that that it is very unlikely that any two atoms are in the same energy level. In the ideal gas, we can calculate the number of levels below, say, $2k_BT$, from $\int_0^{k_\text{max}} g(k)\mathrm{d}k$ with $\hbar^2 k_\text{max}^2/2m = 2k_BT$, giving $2.1 n_Q V$. So we see that n_Q, the "quantum concentration", is a measure of the number of states available, and we can use the approximation $Z_N = (Z_1)^N/N!$ provided $N \ll n_Q V$ (or $n \ll n_Q$). This is the **classical limit**.

We also note that $n_Q \approx 1/\lambda^3$, where λ is the thermal de Broglie wavelength (the wavelength of a particle of energy of order k_BT). So the condition $n \ll n_Q$ is equivalent to saying that the separation of the atoms is much greater than their wavelength, exactly the condition given in last semester's quantum mechanics course for classical behaviour.

The energy and heat capacity derived from (3.69) are unchanged from those of section 3.8, as $N!$ doesn't depend on β.

For the Helmholz free energy, using Stirling's approximation $\ln(N!) \approx N\ln N - N$, we find

$$\begin{aligned}\langle F\rangle &= -k_BT\ln Z_N = -Nk_BT(\ln Z_1 - \ln N + 1)\\ &= -Nk_BT\left[\ln\left(\frac{V}{N}\right) + \ln(g_s n_Q) + 1\right]\\ &= Nk_BT\left[\ln\left(\frac{n}{g_s n_Q}\right) - 1\right].\end{aligned} \tag{3.70}$$

Since n_Q is composed only of constants and T, it is intensive; the number density $n \equiv N/V$ is the ratio of extensive quantities and so is also intensive. Hence F is clearly simply proportional to N, and so extensive as required.

Then

$$\begin{aligned}P &= -\left(\frac{\partial F}{\partial V}\right)_{T,N}\\ &= \frac{Nk_BT}{V}\end{aligned} \tag{3.71}$$

and for the entropy, the *Sackur-Tetrode equation*

$$\begin{aligned}S &= -\left(\frac{\partial F}{\partial T}\right)_{V,N}\\ &= -Nk_B\left[\ln\left(\frac{n}{g_s n_Q}\right) - 1\right] + Nk_BT\frac{1}{n_Q}\frac{\mathrm{d}n_Q}{\mathrm{d}T}\\ &= Nk_B\left[\ln\left(\frac{g_s n_Q}{n}\right) + \frac{5}{2}\right]\end{aligned} \tag{3.72}$$

Since $n \ll n_Q$ if the result is to be valid, S is also positive, as it should be!

The expression for P is clearly experimentally verifiable: it is the ideal gas law. That's good, but we expected to get that. More interestingly the Sackur-Tetrode equation for S can also be checked. First, if we unpick the dependence on V and T, we get

$$S = Nk_B(\ln V + \frac{3}{2}\ln T + \text{const.}) \tag{3.73}$$

which is in accord with the form derived from classical thermodynamics (see here). But more importantly it predicts the *absolute* entropy of a gas at a certain temperature, and this can be checked experimentally too. If we start with the solid at some very low temperature T_0, at which the entropy can be assumed to be very small, and we know the experimental specific heat capacity as a function of temperature and the latent heats of melting and vaporisation, we can numerically calculate the integral

$$\int_{T_0}^{T} \frac{\text{đ}Q}{T} = S(T) - S(T_0) \approx S(T) \tag{3.74}$$

Good agreement is found. An example with numerical details can be found here, from Edward J. Groth of Princeton University.

Finally, we include vibrations and rotations as well as translations: since the one-particle energies are independent and add, $\varepsilon = \varepsilon_{\text{tr}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}}$, the partition functions multiply: $Z_1 = Z_1^{\text{tr}} Z_1^{\text{rot}} Z_1^{\text{vib}}$ (the argument is like that for the N-particle partition function for distinguishable particles and is given here) and so

$$\begin{aligned} Z_N &= \frac{(Z_1^{\text{tr}})^N (Z_1^{\text{rot}})^N (Z_1^{\text{vib}})^N}{N!} = Z_N^{\text{tr}} (Z_1^{\text{rot}})^N (Z_1^{\text{vib}})^N \\ F &= F_{\text{tr}} + F_{\text{rot}} + F_{\text{vib}} \end{aligned} \tag{3.75}$$

and the energy and entropy also add.

It is important to note that, assuming a truly ideal gas which never condenses or solidifies, the Sackur-Tetrode equation is not valid for indefinitely low temperatures. It must be wrong, because as $T \to 0$, $n_Q \to 0$ and $S \to -\infty$. But we know that $S \to 0$ as $T \to 0$, because all the particles occupy the lowest energy level. But of course that is exactly the regime in which $Z_N = (Z_1)^N/N!$ is no longer valid.

For a gas with the density of air at STP, $n \approx 3 \times 10^{25}$ m^{-3}. We have $n_Q \approx n$ for $T \approx 10^{-2}$ K, so real gases are essentially always classical.

An example of a non-classical gas is the conduction electrons in a metal; they are free to move within the metal and can be treated as a dense gas ($n \approx 10^{29}$ m^{-3}), but at room temperature $n_Q \approx 10^{27}$ m^{-3}. So the quantum nature of the electron (specifically the fact that it is a fermion) becomes all important.

3.12.1 Chemical potential of ideal gas

We can find the chemical potential from the Gibbs free energy, is given by $G = E - TS + PV$. For a monatomic ideal gas, $E = \frac{3}{2} N k_B T$ and $PV = N k_B T$. So the sum of these exactly cancels the constant term in the Sackur Tetrode entropy, to give

$$G = -TS + \tfrac{5}{2} N k_B T = -N k_B T \ln\left(\frac{g_s n_Q}{n}\right) \tag{3.76}$$

and the chemical potential, the Gibbs free energy per particle, is

$$\mu = -k_B T \ln\left(\frac{g_s n_Q}{n}\right) \tag{3.77}$$

So in fact, perhaps surprisingly, for an ideal gas in the classical limit, the chemical potential is large and negative. And unlike in classical thermodynamics, we can actually calculate it if we know the temperature and number density.[4]

---

[4] Note we could also get the same result from F, (3.70), using $\mu = \partial F/\partial N|_{T,V}$.

It is important to point out that this chemical potential is relative to the lowest energy state of the system. The zero-point energy of a particle in a box is truly negligible. But in a reaction in which mass is not conserved (which to a varying degree is true of all reactions!) we should write

$$\mu = mc^2 - k_B T \ln\left(\frac{g_s n_Q}{n}\right) \tag{3.78}$$

In cosmological applications, we should note that the Sackur-Tetrode entropy, and hence the expression above, is only correct for non-relative particles.

Consider reactions such as the ionisation of atomic hydrogen

$$\mathrm{H} \rightleftharpoons p + e^-.$$

Equilibrium requires $\mu_H - \mu_p - \mu_e = 0$, or

$$\ln\left(\frac{2n_Q^{(e)}}{n_e}\right) + \ln\left(\frac{2n_Q^{(p)}}{n_p}\right) - \ln\left(\frac{4n_Q^{(H)}}{n_H}\right) + (m_H - m_p - m_e)c^2\beta = 0$$

$$\Rightarrow \quad \frac{n_e n_p}{n_H} = \frac{n_Q^{(p)} n_Q^{(e)}}{n_Q^{(H)}} \mathrm{e}^{\varepsilon\beta} \approx n_Q^{(e)} \mathrm{e}^{\varepsilon\beta} \tag{3.79}$$

We have defined ε as the (negative) energy of the bound state of the electron in hydrogen, -13.6 eV, and given the closeness in mass of p and H we have set the ratio of their quantum concentrations to 1 in the last step. The factors of 2 in the chemical potentials of the proton and electron are the usual spin degeneracies $g_s = 2$ for spin-$\frac{1}{2}$ particles. The factor of 4 for hydrogen is also a degeneracy factor: the total spin of the electron and proton can be $S = 1$ or $S = 0$ with 4 spin states (3+1) in all.

One can take this formula in various directions, but if one assumes the electron density and temperature are known, it gives the ionization fraction n_p/n_H. It can be rewritten in terms of the chemical potential of the electrons (but with the conventional zero of energy, which we will here but not in general write as $\tilde{\mu}_e$) as

$$\frac{n_p}{n_H} = \tfrac{1}{2}\frac{2n_Q^{(e)}}{n_e}\mathrm{e}^{\varepsilon\beta} = \tfrac{1}{2}\mathrm{e}^{(-\tilde{\mu}+\varepsilon)\beta}. \tag{3.80}$$

Astrophysics students will have met (3.79) as the Saha equation. We will meet this problem again in section 3.14.1.

3.13 Using Classical Mechanics

Take-home message: The classical or high-temperature limit of the ideal gas can (nearly) be derived from classical mechanics.

In all of the above, we have counted microstates by considering quantum states of a systems (whether 2-state spin-$\frac{1}{2}$ atoms, rotational and vibrational energy levels, states of a particle in a box....). But statistical physics predates QM, and so do results such as equipartition and the equation of state of an ideal gas. How were microstates originally counted?

We got an idea of the difficulty back in our very first look at the ideal gas, where we had to confront the fact that the position of a particle in a box is, classically, continuous and hence uncountable. The solution there was to divide the volume into tiny cells and accept that our result would depend on the cell size, removing predictive power for absolute entropies but effectively predicting changes.

This is close to the original formulation of the counting of microstates. We work in "phase space", in which the state of a system is specified by the (3D) position and momentum of each particle, 6^N independent coordinates in total. Instead of summing over states we will integrate over phase-space, but we will introduce the concept of an elementary volume in phase-space, so that the number of microstates in a phase-space volume (positions and momenta in some range) is

$$\Omega = \frac{\int \mathrm{d}^{3N}\vec{x} \int \mathrm{d}^{3N}\vec{p}}{h^{3N}} \tag{3.81}$$

Somewhat mysteriously, we have used h^3 for the elementary phase-space volume for a single particle. Note that h has the dimensions of momentum times length.

The energy of the state will be the sum of the kinetic and potential energies; in principle that allows for interactions between particles but we will ignore them, so that the only potential energy comes from an external trap (Warning: V means volume but $V(x)$ is a potential. Sorry....) Then

$$Z_N = \frac{1}{h^{3N}N!} \int \mathrm{d}^{3N}\vec{x} \int \mathrm{d}^{3N}\vec{p}\, \exp\left(-\beta\left(\sum_{i=1}^{3N}\frac{p_i^2}{2m} + V(\{x_i\})\right)\right) \tag{3.82}$$

The justification for (and limitations of) the $1/N!$ are the same as before, and since true indistinguishability is a quantum property, we cannot entirely get away from QM.

For particles in a box, the potential within the box vanishes and positions outside the box are inaccessible, so $\int \mathrm{d}^{3N}\vec{x} = V^N$. So

$$Z_N = \frac{V^N}{h^{3N}N!} \int \mathrm{d}^{3N}\vec{p}\, \exp\left(-\beta\sum_{i=1}^{3N}\frac{p_i^2}{2m}\right) \tag{3.83}$$

There are three ways to tackle this. The simplest is to see it as a product of Gaussians in p_i

$$Z_N = \frac{V^N}{h^{3N}N!}\prod_{i=1}^{3N}\int_{-\infty}^{\infty} \mathrm{d}p_i \exp\left(-p_i^2\frac{\beta}{2m}\right) = \frac{V^N}{h^{3N}N!}\left(2\pi m k_{\scriptscriptstyle B}T\right)^{3N/2} = \frac{Z_1^N}{N!} \tag{3.84}$$

where $Z_1 = V n_{\scriptscriptstyle Q}$, as obtained previously.

This wouldn't work for relativistic particles for which the energy doesn't factorise into a sum of functions of the three components of momentum. So we can instead, for each particle, write $\mathrm{d}^3\vec{p}$ as $4\pi p^2\mathrm{d}p$, then express the $3N$-dimensional integral as a product of N terms, here:

$$Z_N = \frac{1}{N!}\left[\frac{V}{h^3}\int_0^{\infty}\mathrm{d}p\, p^2 \exp\left(-p^2\frac{\beta}{2m}\right)\right]^N = \frac{Z_1^N}{N!} \tag{3.85}$$

This approach is just like the k-space one we used above, with $p = hk/2\pi$ and $g(k)\mathrm{d}k = g(p)\mathrm{d}p$ giving $g(p) = 4\pi V p^2/h^3$.

The final approach, which however is only valid in the same case as the first, where each p_i^2 is summed for all N particles and all 3 directions, is to consider k-space (or rather p-space) in 3N dimensions, using the expression for the surface area of a hypersphere. I will leave it as an exercise for the mathematically-minded reader to check the same result is obtained. (See also the lecture notes of the previous lecturer.)

So we have recovered the same result as before, and all our results for the ideal gas, including the Helmholtz free energy and Sackur-Tetrode entropy (3.72), are recovered, with all the same restrictions on validity ($N/V \ll n_Q$). But I have pulled the wool over your eyes. They only agree if the arbitrary parameter h I introduced in the elementary volume of phase space is actually Planck's constant! Any other choice would correctly predict *changes* in S and F, but not absolute values.

On the problem sheet you will be asked to show that the partition function for a single harmonic oscillator is also reproduced in the high-temperature limit by this classical phase space approach. In this case, because there *is* a potential, the integral $\mathrm{d}^{3N}\vec{x}$ has to be done explicitly and does not simply yield a power of the volume. Since the potential is quadratic in each x_i, though, we just get more Gaussian integrals, and the result is the same as in the high-temperature limit of the QM approach, (3.36): in one dimension

$$Z_1 = \frac{1}{\hbar\omega\beta} \qquad \text{and} \qquad E = k_B T. \tag{3.86}$$

Finally, if you are interested, the concept of the hypersphere can be used to tackle the ideal gas in the microcanonical ensemble. The problem there, if you recall, is that the energy of the whole system is constrained to be fixed, so the particles, while not interacting, cannot simply be treated as independent as they can if they are in contact with a heat bath. In calculating Ω, the integral $\mathrm{d}^{3N}\vec{p}$ has to be carried out with a δ function on the total kinetic energy: effectively this restricts $|\vec{p}|$ to the surface of the hypersphere. Using the surprising result that, for very large N, essentially all the volume of an N-dimensional hypersphere resides at the surface (because of the factor r^{N-1} in the volume element), one integrates instead over all states with energies up to energy E, and the result for $S = k_B \ln\Omega$ is indeed just the Sackur Tetrode one (as a function of $E = 3/2Nk_BT$ rather than T). The previous lecturer's notes (section 3.6) give more detail, but I simply note the result as further proof that for a large system, the microcanonical and canonical approaches give the same result.

3.14 Systems with variable particle number —The Gibbs distribution

- **Mandl** 11.1
- **Bowley and Sánchez** 9.7-9
- **Kittel and Kroemer** 5

Take-home message: The Boltzmann distribution is modified if the particle number can change

First we tackled isolated systems, then we considered systems in contact with a heat bath at temperature T. Now we consider systems which are also in diffusive contact with a particle reservoir at chemical potential μ. In this case the Boltzmann distribution is modified and is called the Gibbs distribution.

This is useful in itself. However just as using the Boltzmann distribution freed us from the constraint that the total energy of all the particles had to add up to a given total energy, and allowed us to consider each particle independently, so using the Gibbs distribution frees us from the constraint that the total numbers of particles in each energy level has to add up to a fixed total, and allows us to treat each energy level independently. Once again we will use the fact that fluctuations in a macroscopic system are negligible to draw conclusions for isolated systems as well.

The temperature is a measure of the decrease in entropy of the reservoir from giving up heat to the system; the chemical potential is a measure of the energy decrease (and entropy increase) of the reservoir from giving up particles to the system (see (2.15)).

We want to find the probability that our system, in contact with the reservoir, will be in a certain microstate i with an energy ε_i and particle number N_i. As usual, recall that neither ε_i nor N_i will be small for a typical system.

The derivation follows that of the Boltzmann distribution closely. Again the probability of the system being in the given microstate depends on the number of microstates available to the reservoir with energy $E_0 - \varepsilon_i$ and particle number $N_0 - N_i$. Expressing the number of microstates as the exponential of the entropy, making a Taylor expansion of the entropy about $S_R(E_0, N_0)$, and expressing the derivatives of the entropy in terms of T and μ thus,

$$\left(\frac{\partial S_R}{\partial E}\right)_{V,N} = \frac{1}{T} \qquad \left(\frac{\partial S_R}{\partial N}\right)_{E,V} = -\frac{\mu}{T}, \tag{3.87}$$

gives

$$p_i = \frac{e^{(\mu N_i - \varepsilon_i)/k_BT}}{\mathcal{Z}} \tag{3.88}$$

with

$$\mathcal{Z} = \sum_j e^{(\mu N_j - \varepsilon_j)/k_BT} \tag{3.89}$$

The new normalisation constant $\mathcal{Z}$ is called the **grand partition function**. Macroscopic functions of state are calculated via ensemble averages as usual; the relevant ensemble in this case is called the **grand canonical ensemble**.

The following properties are easily proved by analogy with the corresponding ones for the Boltzmann distribution (see here and here):

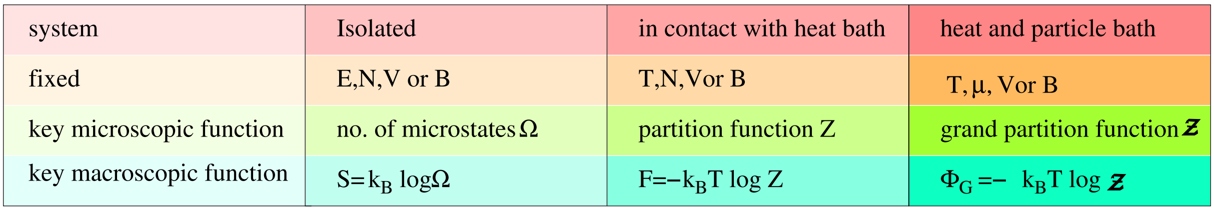
$$\begin{aligned}
\langle N \rangle &= k_BT \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_\beta \\
\langle E \rangle &= -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_\mu + \mu \langle N \rangle \\
\langle S \rangle &= -k_B \sum_i p_i \ln p_i = \frac{1}{T}\left(\langle E - \mu N \rangle + k_BT \ln \mathcal{Z}\right) \\
\Rightarrow \Phi_G \equiv &-k_BT \ln \mathcal{Z} = \langle E - TS - \mu N \rangle . \qquad (3.90)
\end{aligned}$$

The quantity $-k_BT \ln \mathcal{Z}$ is a new thermodynamic potential called the **grand potential**: Mandl gives it the unfortunate symbol Ω but we will use Φ_G like Bowley and Sánchez. (They use Ξ–"Xi"–for $\mathcal{Z}$.) From the fundamental thermodynamic relation we get

$$\mathrm{d}\Phi_G = -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu \tag{3.91}$$

and hence

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} \qquad P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} \qquad N = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}. \tag{3.92}$$



system	Isolated	in contact with heat bath	heat and particle bath
fixed	E,N,V or B	T,N,Vor B	T, μ, Vor B
key microscopic function	no. of microstates Ω	partition function Z	grand partition function $\mathcal{Z}$
key macroscopic function	S= k_B logΩ	F=− k_B T log Z	Φ_G =− k_B T log $\mathcal{Z}$

So whereas in an isolated system the entropy is the key (compare here) and in a system at constant temperature it is the Helmholtz free energy (compare here), here the grand potential is the key to the other functions of state.

The natural variables of the grand potential are T, V and μ. But of these, T and μ are intensive. Like any thermodynamic potential Φ_G itself is extensive, so it must be simply proportional to V, the only extensive one: $\Phi_G = V\phi_G(T,\mu)$.

But

$$\begin{aligned} \phi_G(T,\mu) &= \left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = -P \\ \Rightarrow \Phi_G &= \; -PV. \end{aligned} \tag{3.93}$$

This explains why it is not greatly used in thermodynamics. But the fact that Φ_G is so simple doesn't lessen its formal utility in statistical mechanics.

The grand potential in the case that more than one species is present is

$$\Phi_G \equiv E - TS - \sum_i \mu_i N_i \qquad \text{so} \qquad \mathrm{d}\Phi_G = -S\mathrm{d}T - P\mathrm{d}V - \sum_i N_i \mathrm{d}\mu_i. \tag{3.94}$$

We can use this to prove that μ_i is the Gibbs free energy per particle of species i, as claimed previously ((1.23))

$$G = E - TS + PV = E - TS - (E - TS - \sum_i \mu_i N_i) = \sum_i \mu_i N_i. \tag{3.95}$$

3.14.1 Two examples of the Gibbs Distribution

Take-home message: There is an important distinction between systems in which energy levels can only have one particle in them, and those where they can have many.

Example 1: Sites which bind a single molecule

We first consider sites on a surface which can bind a single molecule only; the energy of the empty site is 0 and that of the occupied site is ε_0 (which can have either sign, but is negative for binding). This example is common in biology, where receptor molecules can be occupied or unoccupied.

The surface is in contact with a gas or a solution with chemical potential μ (the energy drop of the solution when it loses a molecule). What is the grand partition function, and the average occupancy of a site?

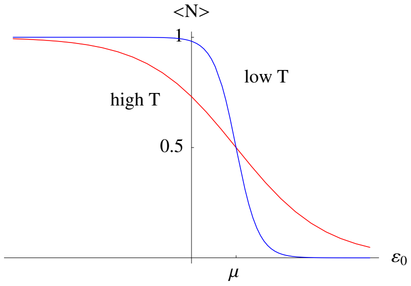
There are only two microstates here: unoccupied, with $N = 0$ and $\varepsilon = 0$, and occupied, with $N = 1$ and $\varepsilon = \varepsilon_0$, so there are only two terms in the grand partition function:

$$\mathcal{Z} = e^0 + e^{(\mu-\varepsilon_0)\beta} = 1 + e^{(\mu-\varepsilon_0)\beta} \tag{3.96}$$

Then

$$\langle N\rangle = -\left(\frac{\partial(-k_BT\ln\mathcal{Z})}{\partial\mu}\right)_\beta = \frac{1}{e^{(\varepsilon_0-\mu)\beta}+1}. \tag{3.97}$$

Below we plot the average occupancy as a function of ε_0, the energy of the level in question. We see that $\langle N\rangle$ is always less than 1, as it must be. If a level lies above the chemical potential, $\varepsilon_0 > \mu$ then it is less likely to be occupied, since it is energetically more favourable for the molecule to remain in solution. Conversely if $\varepsilon_0 < \mu$ then it is more likely to be occupied, since that is the energetically favourable configuration. As always, it is the temperature which determines the likelihood of the less favourable configuration obtaining. At zero temperature, the distribution becomes a step function, with $\langle N\rangle = 1$ if $\varepsilon_0 < \mu$ and $\langle N\rangle = 0$ if $\varepsilon_0 > \mu$.

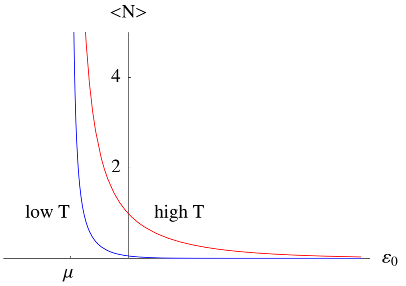


Example 2: sites which bind many molecules

This is less realistic, but we imagine a site which can have any number of molecules occupying it, with energy ε_0 per molecule. There are then infinitely many terms in the grand partition function which form a geometric series:

$$\begin{aligned}\mathcal{Z} &= e^0 + e^{(\mu-\varepsilon_0)\beta} + e^{2(\mu-\varepsilon_0)\beta} + \ldots = \frac{1}{1-e^{(\mu-\varepsilon_0)\beta}}\\ \langle N\rangle &= \frac{1}{e^{(\varepsilon_0-\mu)\beta}-1}.\end{aligned} \tag{3.98}$$

Below we plot the average occupancy as a function of ε_0, the energy of the level in question. Unlike the first example, there is no limit to $\langle N\rangle$. Thus it doesn't make sense to consider states with $\varepsilon_0 < \mu$, as their occupancy will be infinite. (The formula above for $\langle N\rangle$ is no longer valid in that case.) For ε_0 close to μ the occupancy will be high, and it falls off as ε_0 increases. The rapidity of the drop depends on temperature; for $T = 0$ only a level with $\varepsilon_0 = \mu$ would have non-zero occupancy.



Chapter 4

Quantum Gases

4.1 Bosons and fermions

Take-home message: All particles in nature are either bosons or fermions. Their statistical properties are very different: no two fermions can be in the same state, but there is no such restriction on bosons.

- **Mandl** 9.2
- **Bowley and Sánchez** 10.2

Bosons are particles with integer spin:
spin 0: ^{1}H and ^{4}He in ground state, pion, Higgs boson
spin 1: ^{1}H and ^{4}He in first excited state, ρ meson, photon, W and Z bosons, gluons
spin 2: ^{16}O in ground state, graviton.

Fermions are particles with half-integer spin:
spin $\frac{1}{2}$: ^{3}He in ground state, proton, neutron, quark, electron, neutrino
spin $\frac{3}{2}$: ^{5}He in ground state, Δ baryons (excitations of the proton and neutron)

First a note on notation. When we talk about the “spin” of a composite particle we mean its total angular momentum, and we usually use the symbol J rather than S. Last semester you met J as the (quantised, vector) sum of orbital and spin angular momentum for the electron, but more generally it is the (quantised, vector) sum of all the spins and all the orbital angular momenta of all the constituents.

The basic building blocks of atoms are all fermions, while the force carriers (photon, gluon, W,Z) and the Higgs are bosons. The rules of addition of angular momentum mean that two spin-$\frac{1}{2}$ particles with no orbital angular momentum can either have total angular momentum $J = 0$ or 1; if we add a third, we have $J = \frac{1}{2}$ or $\frac{3}{2}$; a fourth gives $J = 0, 1$ or 2, and so on. Adding in orbital angular momentum, which is integer, gives more possibilities, but J is still always half integer for an odd number of spin-$\frac{1}{2}$ particles and integer for an even number. So composite particles (nuclei, atoms, molecules) made of an odd number of protons, neutrons and electrons are also fermions, whereas those made of an even number are bosons. Note that a particle is either a fermion or boson. Excitations of composite partcles (nuclei, atoms) can change the spin only by an integer amount and so don't change the its nature.

Fermions obey the **Pauli exclusion principle**: no more than one fermion can occupy a single quantum state. (The value of the spin quantum number m_s is part of the description of the state; if that is ignored then two spin-$\frac{1}{2}$ or four spin-$\frac{3}{2}$ particles can occupy the same *spatial* state.) This is the basis of atomic structure and the periodic table, it explains the properties of metals and of white dwarves and neutron stars.

The "grown-up" version of the Pauli exclusion principle is that the overall wave function of a system of identical fermions must be antisymmetric under exchange of any pair. For two spin-$\frac{1}{2}$ particles in the same spatial state (say the $1s$ state of helium) the overall wave function must be

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, m_1, m_2) = \tfrac{1}{\sqrt{2}}\phi_{1s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)(\uparrow\downarrow - \downarrow\uparrow) \tag{4.1}$$

The spatial part is symmetric but the spin part is antisymmetric. (This corresponds to overall spin 0). If we try to construct a state with three particles in the same spatial state we can't do it, there is no state $(\uparrow\downarrow\uparrow - \ldots)$ which changes sign when we interchange any pair of particles. So the Pauli exclusion principle follows from the requirement for antisymmetry.

It is possible to have a 2-fermion spin-state such as $\uparrow\uparrow$ (spin-1) but then the particles have to be in different spatial states, eg

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, m_1, m_2) = \tfrac{1}{\sqrt{2}}\Big(\phi_{1s}(\mathbf{r}_1)\phi_{2s}(\mathbf{r}_2) - \phi_{2s}(\mathbf{r}_1)\phi_{1s}(\mathbf{r}_2)\Big)\uparrow\uparrow \tag{4.2}$$

There is no exclusion property for identical bosons, but there *is* a restriction on their wave function: it must be symmetric under exchange of any pair. So for spinless bosons

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3 \ldots) = \tfrac{1}{\sqrt{2}}\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\phi(\mathbf{r}_3)\ldots \tag{4.3}$$

is a perfectly acceptable wave function and there is no Pauli exclusion principle. For spin-1 bosons we have to ensure that the overall space-spin wave function is symmetric, but the details are not important here.

So bosons are free to (indeed, other things being equal, "prefer" to) crowd into the same quantum state. This explains the spectrum of black-body radiation and the operation of lasers, the properties of liquid ^{4}He and superconductors.

The need for the wave function to be either symmetric or antisymmetric for identical particles stems from the very meaning of "identical": nothing observable can change if we swap the particles. In particular

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, m_1, m_2)|^2 = |\Psi(\mathbf{r}_2, \mathbf{r}_1, m_2, m_1)|^2 \tag{4.4}$$

This implies that

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, m_1, m_2) = \mathrm{e}^{i\alpha}\Psi(\mathbf{r}_2, \mathbf{r}_1, m_2, m_1) \tag{4.5}$$

for some real phase α. But two swaps have to return us to the same state without any phase change at all, so $2\alpha = 2n\pi$. Only $\alpha = \pi$ and $\alpha = 2\pi$ are possible.

4.2 The ideal gas of bosons or fermions: beyond the classical approximation

Take-home message: Where the number of available states approaches the number of particles in the system, the properties of the gas will depend on whether multiple occupancy is allowed (bosons) or not (fermions).

- **Mandl** 11.2,11.4,11.5
- **Bowley and Sánchez** 10.2-3

When we derived the properties of the ideal gas previously, using the classical approximation for the partition function $(Z_1)^N/N!$, our results were only valid if the number of available single-particle levels greatly exceeded the number of particles in the gas ($n_Q \gg n$). This was because we knew that we were not treating states with more than one particle in them correctly. Now we know that if the gas particles are fermions, that isn't even possible, so we need a new approach. What we do is lift the restriction that the number of particles in the gas is fixed, and use the Gibbs distribution instead of Boltzmann.

In a previous section we looked at the grand partition function for a single state which could accept either only one, or many, particles. These will be our starting points for the consideration of gases of fermions or bosons in the regime in which we cannot ignore the possibility of multiple occupancy of states (bosons) or restrictions in the available states because they are already occupied (fermions).

We then find that rather than focus on a single particle in the gas, it is easier to focus on what is happening in a single energy level. Then we can write, using r to label the energy level, not the particle

$$\mathcal{Z} = \mathcal{Z}_1\mathcal{Z}_2\mathcal{Z}_3\ldots = \prod_r \mathcal{Z}_r \qquad \text{where} \qquad \mathcal{Z}_r = 1 + \mathrm{e}^{(\mu-\varepsilon_r)\beta} + \mathrm{e}^{2(\mu-\varepsilon_r)\beta}\ldots \tag{4.6}$$

(For fermions the sum in $\mathcal{Z}_r$ is restricted to the first two terms.)

Perhaps this step is not obvious. Each term in each $\mathcal{Z}_r$ corresponds to 0, 1, 2, 3... particles in that state. So $\mathcal{Z}$ is then a sum of many terms, each one with a particular occupancy of each level $(n_1, n_2, n_3) \equiv \{n_i\}$. These are exactly the microstates of the whole system when N is not fixed. The argument is closely analogous to that for the factorisation of the (ordinary) partition function for independent particles, section 3.9.

Note that we ignoring conventional interactions, in that we are summing over the single-particle states which by definition are calculated without considering interactions between particles. But it wouldn't be quite correct to say that we are treating the particles as independent, because their boson or fermion nature will be have an important influence on the multi-particle system.

Since the log of a product is the sum of logs of the individual terms, the grand potential Φ_G, the energy, the particle number and the entropy all consist of sums of the contributions from each level: $\langle N\rangle = \sum_r \langle N_r\rangle$, $\langle E\rangle = \sum_r \langle N_r\rangle\,\varepsilon_r$ etc.

We are going to introduce a new notation here. To reflect the fact that $\langle N_r\rangle$, the occupancies of individual level, are microscopic, we are going to use small letters, and because the $\langle\ldots\rangle$ notation is clumsy we will use an overline, also commonly used for averages: so $\langle N_r\rangle \equiv \overline{n}_r$ and $\langle N\rangle = \sum_r \overline{n}_r$ etc. This is the same notation as Mandl, and as Dr Galla. Dr Xian in PHYS20252 uses f. There is potential for confusion with the particle density (which Dr Galla called ρ!) but I hope forewarned is forearmed.

Furthermore we have already found the single-level grand partition functions $\mathcal{Z}_r$ and the average occupancies $\overline{n}_r$: for fermions, which obey the Pauli exclusion principle:

$$\mathcal{Z}_r = 1 + e^{(\mu-\varepsilon_r)\beta} \qquad\qquad \overline{n}_r = \frac{1}{e^{(\varepsilon_r-\mu)\beta}+1} \tag{4.7}$$

and for bosons, which don't:

$$\mathcal{Z}_r = \frac{1}{1-e^{(\mu-\varepsilon_r)\beta}} \qquad\qquad \overline{n}_r = \frac{1}{e^{(\varepsilon_r-\mu)\beta}-1}. \tag{4.8}$$

(see section 3.14.1).

For a gas the sum over discrete energy levels is replaced by an integral over the wave number k, weighted by the density of states.

$$\langle N\rangle = \int_0^\infty g(k)\overline{n}(k)\mathrm{d}k \qquad \langle E\rangle = \int_0^\infty g(k)\varepsilon(k)\overline{n}(k)\mathrm{d}k \tag{4.9}$$

where $\varepsilon(k) = \hbar^2 k^2/2m$ for non-relativistic particles and

$$\overline{n}(k) = \frac{1}{e^{(\varepsilon(k)-\mu)\beta} \pm 1} \qquad \text{for} \left\{ \begin{matrix} \text{fermions} \\ \text{bosons} \end{matrix} \right\} \tag{4.10}$$

Note that for bosons, μ must be less than the energy of the lowest level (zero for most purposes) but for fermions μ can be (and often will be) greater than 0.

The Gibbs distribution assumes variable particle number and constant chemical potential (as well variable energy and constant temperature). However we knew that for a large system, fluctuations are small, and the results will be essentially the same as the more difficult problem of an gas with fixed particle number. To cast it in this form, we use the expressions of (4.9) to find the value of μ which gives the desired N. Then we can also find the average energy per particle. This is conceptually simple, but not usually possible analytically except in certain limits. In the next subsection we will recover the classical ideal gas.

4.2.1 The classical approximation again

Take-home message: The Gibbs distribution gives an alternative way of treating the ideal gas in the classical limit.

Here we rederive our previous results for the ideal gas regarding the particle number as variable also, fixing instead the chemical potential.

From the previous sections on the Gibbs distribution and the ideal gas of bosons or fermions, we have

$$\begin{aligned} \Phi_G &\equiv -k_BT\ln\mathcal{Z} \\ &= -k_BT\sum_r \ln\mathcal{Z}_r \qquad\qquad \text{using } \mathcal{Z} = \textstyle\prod_r \mathcal{Z}_r \\ &= \mp k_BT\sum_r \ln\left(1 \pm e^{(\mu-\varepsilon_r)\beta}\right) \end{aligned} \tag{4.11}$$

where r labels the single particle energy levels, and the signs are for fermions and bosons respectively.

Now imagine that $e^{\mu\beta} \ll 1$, which requires μ to be large and negative. Never mind for a moment what that means physically. Then, using $\ln(1+x) \approx x$ for small x, we get

$$\begin{aligned} \Phi_G &= -k_BT\sum_r e^{\mu\beta}e^{-\varepsilon_r\beta} \\ &= -k_BTe^{\mu\beta}Z_1(T) \end{aligned} \tag{4.12}$$

where Z_1 is the one-particle translational partition function (not grand p.f.) for an atom in an ideal gas. As we calculated previously, $Z_1(T) = Vg_s n_Q(T)$

From Φ_G we can find the average particle number:

$$\begin{aligned} N &= -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V} \\ &= e^{\mu\beta} Z_1 \end{aligned} \tag{4.13}$$

and solving for μ we get

$$\mu = -k_B T \ln(Z_1/N) = -k_B T \ln\left(\frac{g_s n_Q}{n}\right) \tag{4.14}$$

So now we see that μ large and negative requires $n \ll n_Q$ or far fewer particles than states—exactly the classical limit as defined before. We obtained this result previously, see (3.77).

Finally, since $\Phi_G = E - TS - \mu N = F - \mu N$, we have

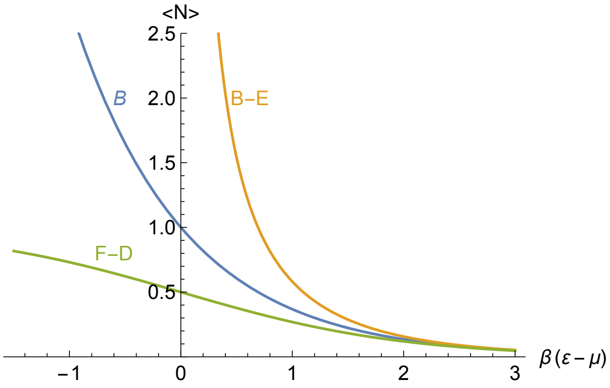
$$\begin{aligned} F &= \Phi_G + \mu N \\ &= -Nk_B T - Nk_B T \ln(Z_1/N) \\ &= -Nk_B T \left(\ln(Z_1/N) + 1\right) \end{aligned} \tag{4.15}$$

However this is exactly what we get from $F = -k_B T \ln Z_N$ with $Z_N = (Z_1)^N/N!$. Thus we recover all our previous results.

We can also look at the occupancy $\overline{n}(\varepsilon)$: for large negative μ,

$$\overline{n}(\varepsilon) = \frac{1}{\mathrm{e}^{(\varepsilon-\mu)\beta}} \approx \mathrm{e}^{\mu\beta}\mathrm{e}^{-\varepsilon\beta} = N\frac{\mathrm{e}^{-\varepsilon\beta}}{Z_1} \tag{4.16}$$

which is the Boltzmann distribution as expected. The three distributions, Bose-Einstein (orange), Boltzmann (blue) and Fermi-Dirac (green) are plotted as a function of $(\varepsilon - \mu)\beta$ below:



It is reassuring that we can recover the classical ideal gas predictions of course. We can also look at the first corrections in an expansion in the density (n/n_Q). For a classical gas this is called a virial expansion; for a van der Waal gas, for instance,

$$PV = Nk_B T\left(1 + \left(b - \frac{a}{RT}\right)\frac{N}{V} + \dots\right)$$

where b is the excluded volume due to finite molecular size and a arises from attractive interactions.

But even for an ideal (zero electrostatic interactions, point-like) Bose or Fermi gas such terms appear. An example on the problem sheets asks you to show that, for for fermions and bosons respectively,

$$PV = Nk_BT\left(1 \pm \frac{n}{4\sqrt{2}g_s n_Q} + \ldots\right). \tag{4.17}$$

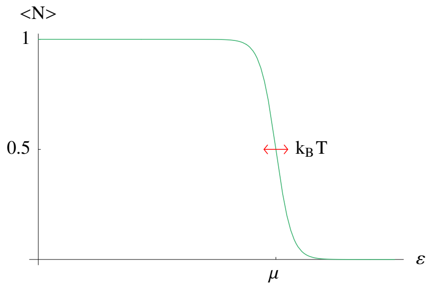
So for fermions the pressure is larger than expected, consistent with a reluctance to occupy the same space (like a non-zero b). This isn't too surprising. More surprising perhaps is the fact that for bosons, the pressure is *smaller*, as if there were attractive interactions. Whereas fermion "like" to keep apart, bosons are gregarious!

4.3 The ideal Fermi Gas

4.3.1 Electrons in a metal

Take-home message: The properties of Fermi gases such as electrons in metals and neutron stars are dramatically different from ideal classical gases.

- **Mandl** 11.5
- **Bowley and Sánchez** 10.4.2



We have already seen that for electrons in metal, the number of states with energies of order k_BT is much less that the number of electrons to be accommodated. Because electrons are fermions, they can't occupy the same levels, so levels up to an energy far above k_BT will need to be filled. The occupancy is given by (4.10) for fermions

$$\overline{n}(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)\beta} + 1} \tag{4.18}$$

which is plotted above.

At zero temperature, it is clear what the ground state—the state of lowest possible energy—of a fermion gas must be. All energy levels will be occupied (singly-occupied if we regard the spin as part of the specification of the state) up to a maximum, and all higher levels will be unoccupied. The occupation function $\overline{n}(\varepsilon)$ becomes a step function—one up to a certain value of ε and zero thereafter. Do our results bear this out?

Considering $\overline{n}(\varepsilon)$, we see that the limit $T \to 0$, $\beta \to \infty$ needs to be taken rather carefully. Clearly it will depend on the sign of $\varepsilon - \mu$. If $\varepsilon < \mu$ then the argument of the exponential is very large and negative and the exponential itself can be ignored in the denominator, simply giving $\overline{n}(\varepsilon) = 1$. But if $\varepsilon > \mu$, the argument of the exponential is very large and positive and the "+1" can be ignored in the denominator, so that $\overline{n}(\varepsilon) \to e^{-(\mu-\varepsilon)\beta} \to 0$. So

$$\overline{n}(\varepsilon) \to \begin{cases} 1 & \text{for } \varepsilon < \mu \\ 0 & \text{for } \varepsilon > \mu \end{cases} \tag{4.19}$$

So in fact μ is the energy of the highest occupied state at zero temperature. This is also known as the *Fermi energy*, ε_F, and indeed the two terms, "chemical potential" and "Fermi energy" are used interchangeably for a Fermi gas.[1] The value of k corresponding to this energy, k_F, is referred to as the "Fermi momentum" (albeit that should really be $\hbar k_F$). A gas like this where only lowest levels are occupied is called a *degenerate* gas: this is a different usage from "degenerate" to mean "equal energy". The filled levels are called the *Fermi sea* and the top of the sea is called the *Fermi surface*.

So what is the value of the Fermi energy at zero temperature? It is simply fixed by N, which we set equal to $\langle N\rangle$:

$$\begin{aligned} N =& \int\limits_0^\infty g(k)\overline{n}(k)\mathrm{d}k = \int\limits_0^{k_F} g(k)\mathrm{d}k \\ =& \frac{g_s V}{2\pi^2}\int\limits_0^{k_F} k^2 \mathrm{d}k = \frac{g_s V}{2\pi^2}\frac{k_F^3}{3} \end{aligned} \tag{4.20}$$

so, with $g_s = 2$ and $= \hbar^2 k_F^2/2m$ for non-relativistic electrons, and $n = N/V$

$$k_F = (3\pi^2 n)^{1/3} \qquad \text{and} \qquad \varepsilon_F = \frac{(3\pi^2\hbar^3 n)^{2/3}}{2m} \tag{4.21}$$

The energy is given by

$$E = \int\limits_0^\infty g(k)\overline{n}(k)\varepsilon(k)\mathrm{d}k = \frac{\hbar^2}{2m}\int\limits_0^{k_F} k^2 g(k)\mathrm{d}k = \frac{g_s V\hbar^2}{4\pi^2 m}\frac{k_F^5}{5} = \tfrac{3}{5}N\varepsilon_F \tag{4.22}$$

Note all these depend, as we expect, only on N/V and not on V alone. ε_F is intensive, and $E \propto N$. For copper, $\varepsilon_F = 7$ eV.

Note too that though we have written our integrals over wave number k, we can equally switch to ε as the variable, using the density of space in energy from section 3.51, eg:

$$N = \int\limits_0^\infty g(\varepsilon)\overline{n}(\varepsilon)\mathrm{d}\varepsilon = \frac{g_s V(2m)^{3/2}}{4\pi^2\hbar^3}\int\limits_0^{\varepsilon_F} \varepsilon^{1/2}\mathrm{d}\varepsilon = \frac{g_s V}{6\pi^2}\left(\frac{2m\varepsilon_F}{\hbar^2}\right)^{3/2} \tag{4.23}$$

which is the same as before. Generally I prefer only to remember $g(k)$ and to work out $g(\varepsilon)$ if required. After all $g(k)$ only depends on the dimension of space, usually 3D in practice, while $g(\varepsilon)$ differs depending on whether the particles are relativistic or not.[2]

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[1] Actually sometimes the "Fermi energy" is used exclusively for the zero-temperature chemical potential, the highest filled energy, and "Fermi level" is used for the energy with an occupancy of 0.5, which is $\varepsilon = \mu$. We will use Fermi energy at or near zero temperature, and chemical potential where the occupancy deviates substantially from a step function.

[2] Note the warning about the difference in notation for $g(\varepsilon)$ between Dr Xian and myself contained at the end of section 3.8.1. He divides out the volume V.

All of the above is at zero temperature. At finite temperatures, the picture will change—but not by as much as you might expect. Thermal excitations can only affect levels within a few k_BT of ε_F. But at room temperature, $k_BT = 0.025$ eV. For k_BT to equal ε_F would need $T \sim 80,000$ K, a temperature at which the metal would have vaporised. ($T_F = \varepsilon_F/k_B$ is called the Fermi temperature, but in no sense is it a real temperature, it's just a way of expressing the Fermi energy in other units.) We can see from (4.18) that $\overline{n}(k)$ will still essentially be 0 or 1 unless $|\varepsilon - \varepsilon_F|$ is of the order of k_BT. This is shown in the figure at the top of the section.

As the temperature rises, the Fermi energy doesn't remain constant, though it doesn't change much initially. Again we find it from requiring the electron density to be correct,

$$\frac{N}{V} = \frac{1}{V}\int_0^\infty g(k)\overline{n}(k)\mathrm{d}k = \frac{g_s}{2\pi^2}\int_0^\infty \frac{k^2}{\mathrm{e}^{(\hbar^2k^2/2m-\mu)\beta}+1}\mathrm{d}k = \frac{1}{2}\left(\frac{2m}{\hbar^2\beta}\right)^{3/2}\frac{1}{\pi^2}\int_0^\infty \frac{x^{\frac{1}{2}}}{\overline{z}\mathrm{e}^x+1}\mathrm{d}x \tag{4.24}$$

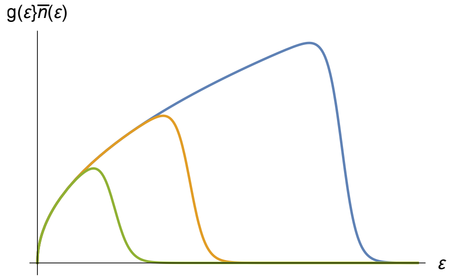
where $\overline{z} = \mathrm{e}^{-\mu\beta}$ and we have made the change of variable to the dimensionless $x \equiv \varepsilon(k)\beta$:

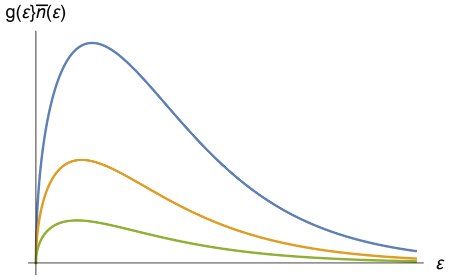
$$x = \frac{\hbar^2\beta}{2m}k^2 \qquad k = \left(\frac{2m}{\hbar^2\beta}\right)^{1/2} x^{1/2}, \qquad \mathrm{d}k = \frac{1}{2}\left(\frac{2m}{\hbar^2\beta}\right)^{1/2} x^{-1/2}\,\mathrm{d}x \tag{4.25}$$

Rearranging, and setting $g_s = 2$, we get

$$\boxed{F(\overline{z}) \equiv \int_0^\infty \frac{x^{\frac{1}{2}}}{\overline{z}\mathrm{e}^x+1}\mathrm{d}x = 4\pi^2\, n\left(\frac{\hbar^2\beta}{2m}\right)^{3/2} = \frac{\sqrt{\pi}}{2}\frac{n}{2n_Q}.} \tag{4.26}$$

The integrand is shown, as a function of energy at fixed temperature, on the left for three positive values of μ and on the right for $\mu = 0$ and two negative values of μ; the area under the curve is proportional to N/V. In each plot blue, orange and green are in decreasing order of μ; the horizontal and vertical scales on the left are much larger than on the right.





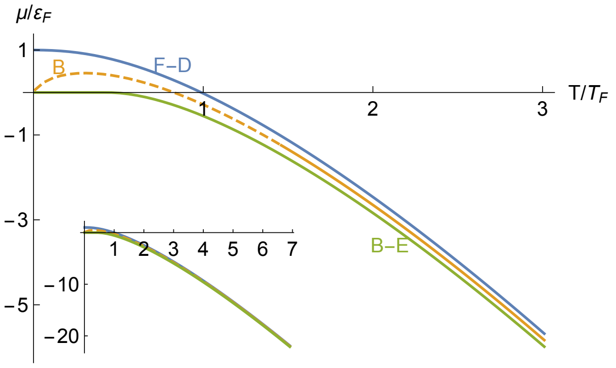
The area under the curves, hence the function $F(\overline{z})$, can be obtained by numerical integration. Then $\overline{z}$, and hence μ, can can be chosen to obtain the correct particle number density.[3]

Note that the n/n_Q is greater than 1 for copper at room temperature. $F(\overline{z})$ becomes large as $\overline{z} \to 0$, $\mu \gg k_BT$, which fits this situation. Conversely for $\overline{z} \gg 1$, corresponding to large negative μ, the integral tends to $\sqrt{\pi}/2\overline{z}$ and we recover the classical limit as in the last section, (4.14).

Below is plotted (in blue, labelled "F-D") the ratio of the chemical potential to the zero-temperature Fermi energy, as a function of temperature in units of the Fermi temperature. Also shown (in orange, labelled "B") is the classical approximation (4.14) (ignore for the moment the green curve labelled "B-E"):

---

[3] Why have I used $\overline{z}$ as the variable? Well it is more common to define $z = \mathrm{e}^{\mu\beta}$—it even has a name, the *fugacity*—so my variable is $\overline{z} = 1/z$. But I thought that to write z^{-1} would be ugly.... $F(\overline{z})$ is defined in terms of so-called polylogarithms of z, but the details will not concern us.

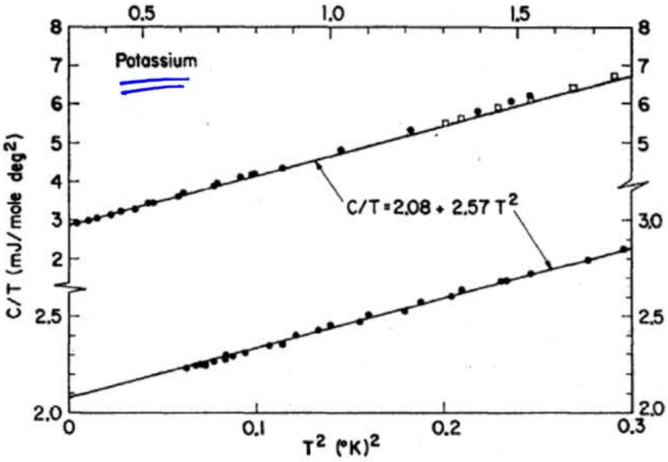


The number density n doesn't appear because it has been eliminated in terms of ε_F. The classical approximation slowly approaches the full expression as $T \to \infty$, as can be seen in the inset panel.[4]

The fact that thermal fluctuations affect only a small fraction of all the electrons has a number of consequences. For instance the electronic heat capacity is much less than the $\frac{3}{2}Nk_BT$ predicted by equipartition. Thermal excitations can only affect states with energies of the order of k_BT below the Fermi surface, roughly a fraction k_BT/E_F of the total, and their excess energy is about k_BT. So the extra energy above the zero temperature value of $\frac{3}{5}NE_F$ is of order $N(k_BT)^2/E_F$ and the electronic heat capacity is of order

$$C_V \propto Nk_B\frac{T}{T_F}. \tag{4.27}$$

A more careful calculation gives the constant of proportionality to be $\pi^2/2$. This linear rise with temperature can be seen at very low temperatures; at higher temperatures the contribution of lattice vibrations dominates, and we will explore this later.



Data from Lien and Phillips, Phys. Rev. 133 (1964) A1370

The figure above shows the molar heat capacity as a function of temperature for potassium.[5] What is actually plotted is C/T against T^2, so the straight-line implies

$$C = (2.08\ \mathrm{mJK^{-2}})T + (2.57\ \mathrm{mJK^{-4}})T^3. \tag{4.28}$$

---

[4] For a non-relativistic gas in 2D, the relation between μ and N can be solved analytically, and a similar-looking graph is obtained.

[5] The bottom line shows the range $0 < T^2 < 0.3$, with the scale on the bottom of the figure; the upper line shows the continuation of the same function for $0.3 < T^2 < 1.8$, with the scale on the top.

The prediction of the model above would give the first number as 1.7 mJK^{-2} for potassium with a Fermi temperature of 2.4×10^4 K, which is good to 20% — not bad considering how simple the model is.

Similar considerations allow predictions to be made about the thermal conductivity; normalising by the electrical conductivity to cancel the dependence on the collision time gives the Wiedemann-Franz law:

$$\frac{\kappa}{\sigma} \propto T \tag{4.29}$$

These will be covered in much more detail in PHYS20252.

Most of the resistance to compression of metals is due to the fact that, if the volume is reduced, the energy of all the single-electron states increases, increasing the electronic internal energy. This same effect turns out to stabilise white dwarf stars against gravitational collapse, as we will now see.

A very different substance whose behaviour is pretty well described as degenerate Fermi "gas" is liquid ^{3}He at sub-Kelvin temperatures, and indeed the heat capacity is nicely linear. However below 2 mK the behaviour changes and is better described by a bosonic liquid exhibiting superfluidity! The picture is that the fermion atoms pair up to form bosons, which can condense—as we will see later.

4.3.2 White dwarf stars

In the formation of a main sequence star, a cloud of hydrogen collapses till it is dense enough for nuclear fusion to occur; equilibrium is obtained when the outward pressure of the hot plasma balances the gravitational attraction. Energy is radiated but fusion generates more. When the hydrogen fuel is mostly used up, however, this equilibrium is lost. Further nuclear processes can also occur, raising the central temperature and causing the star to become a red giant; however when all such processes are exhausted the cooling star will start to collapse. For a star of the size of the sun, the collapse continues until the increasing density and decreasing temperature causes the electron to cease to be a classical gas, being better described by the Fermi-Dirac distribution. Eventually, though still very hot ("white hot") the density is such that $\mu \gg k_B T$ and the electron gas is well described by a "zero-temperature" degenerate electron gas, with the gravitational attraction balanced by the degeneracy pressure.

The pressure of a degenerate Fermi gas can be obtained from the grand potential; since at zero temperature $\Phi_G = E - \mu N = E - N\varepsilon_F$, from (4.22) we have

$$PV = -\Phi_G = -\left(\tfrac{3}{5} - 1\right) N\varepsilon_F = \tfrac{2}{5} N\varepsilon_F \qquad \Rightarrow \qquad P = \tfrac{2}{5} n\varepsilon_F = \frac{\hbar^2 (3\pi^2)^{2/3}}{5m_e} n^{5/3}. \tag{4.30}$$

Note in passing that $PV = \frac{2}{3}E$, as for a classical ideal gas! This holds even at finite temperature, as you will be asked to show on the problems sheets. The origin of both the internal energy and the pressure is quite different though.

We will assume that the composition of the star is constant, so that there is a constant ratio between the electron density and the matter density, $\rho \propto n$. For hydrogen the constant of proportionality would just be m_H, whereas for heavier nuclei it will be around 2 amu or slightly more (roughly, one proton and one neutron per electron). It turns out that, apart from the total mass, the composition is the only thing that distinguishes one white dwarf from another. Lighter stars are mostly carbon and oxygen, heavier ones have heavier elements up to iron.

Within a star the density, Fermi energy and and pressure will vary with radius. For equilibrium, the pressure difference across a spherical shell at r has to exactly balance the weight:

$$4\pi r^2(P(r) - P(r + \mathrm{d}r)) = 4\pi r^2 \mathrm{d}r \frac{G\rho(r)M(r)}{r^2}$$
$$\Rightarrow \quad \frac{\mathrm{d}P}{\mathrm{d}r} = -\frac{G\rho(r)}{r^2} \int_0^r 4\pi r'^2 \rho(r')\mathrm{d}r' \tag{4.31}$$

Writing $P(r) = C\rho(r)^{5/3}$ allows us to turn this into a second-order non-linear differential equation for the density $\rho(r)$. And with some manipulation that we won't go into here (Google "polytrope" if you are interested), it can be shown that the solution can be cast in terms of the average density and a universal dimensionless function of the scaled variable r/R, where R is the radius of the star:

$$\rho(r) = \overline{\rho}\, f(r/R) \tag{4.32}$$

Without going into the details of that function, we can none-the-less derive an interesting consequence: a mass-radius relation for white dwarf stars. We return to Eq. (4.31) and integrate to obtain the pressure difference from the centre to the surface $r = R$ at which $P(R) = 0$:

$$-\int_0^R \frac{\mathrm{d}P}{\mathrm{d}r}\mathrm{d}r = P(0) = \int_0^R \frac{G\rho(r)M(r)}{r^2}\mathrm{d}r \tag{4.33}$$

Then using (4.32), which also implies a universal function g for the mass $M(r)$ (which is obviously related to f but we don't need the details):

$$M(r) = Mg(r/R), \qquad \text{where} \quad \tfrac{4}{3}\pi R^3 \overline{\rho} = M; \tag{4.34}$$

and looking back to (4.30) we see that the central pressure is proportional to $\overline{\rho}^{5/3}$, giving

$$\overline{\rho}^{5/3} \propto GM\overline{\rho} \int_0^R \frac{f(r/R)g(r/R)}{r^2}\mathrm{d}r = \frac{GM\overline{\rho}}{R} \int_0^1 \frac{f(x)g(x)}{x^2}\mathrm{d}x \tag{4.35}$$

The integral is universal and dimensionless; ie just a number which is the same for all white dwarfs of a similar composition. Then we canel one power of $\overline{\rho}$ from either side to get

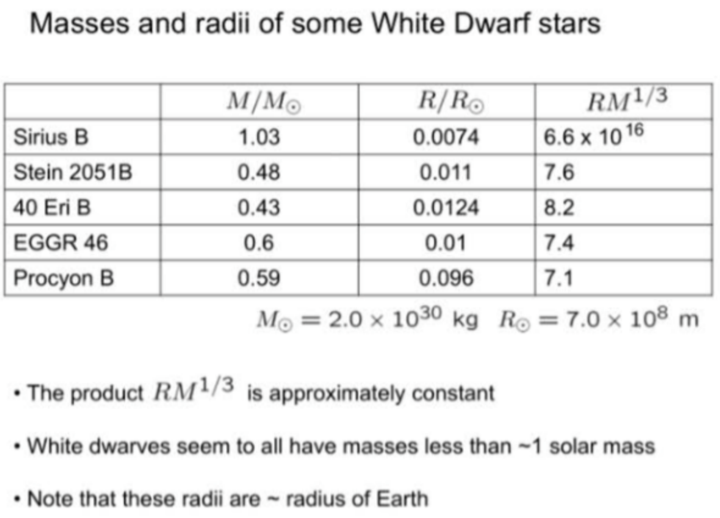
$$(M/R^3)^{2/3} \propto M/R \Rightarrow MR^3 = \text{constant} \tag{4.36}$$

This relationship is pretty well satisfied by white dwarf stars of masses less than one solar mass (see table below). Note that it implies that the more massive the star, the smaller the radius. For 1 solar mass, the radius is about that of the earth!

It looks like there would be no upper limit on the mass, but we have assumed that the electrons are non-relativistic, and as the Fermi energy approaches $m_e c^2$ this is no longer valid. In the highly relativistic regime the pressure is proportional to $n^{4/3}$ (see problem sheets), and doesn't grow fast enough as the star shrinks to stabilise it (check it in (4.36): the radius cancels). So there is an upper bound to the mass of a white dwarf of about 1.4 solar masses—the Chandrasekhar limit. This involves a pleasing combination of microscopic and macroscopic parameters with a numerical factor which is of order 1:

$$\frac{(\hbar\, c/G)^{3/2}}{(2m_p)^{\,2}} \sim M_{\odot}$$

Above that an even more compact object sustained by the degeneracy pressure of neutrons can form, but that again has an upper mass limit of about 2 solar masses (and radius of about 10 km). Beyond that, only black holes are possible...



Masses and radii of some White Dwarf stars

	$M/M_\odot$	$R/R_\odot$	$RM^{1/3}$
Sirius B	1.03	0.0074	6.6 x 10^{16}
Stein 2051B	0.48	0.011	7.6
40 Eri B	0.43	0.0124	8.2
EGGR 46	0.6	0.01	7.4
Procyon B	0.59	0.096	7.1

$M_\odot = 2.0 \times 10^{30}$ kg $R_\odot = 7.0 \times 10^{8}$ m

- The product $RM^{1/3}$ is approximately constant
- White dwarves seem to all have masses less than ~1 solar mass
- Note that these radii are ~ radius of Earth

table from J Forshaw, PHYS30151

4.4 The ideal Bose Gas

4.4.1 Photons and Black-body radiation

Take-home message: Black-body radiation is an example of a Bose gas

- **Mandl** 10.3-5
- **Bowley and Sánchez** 8.5

Classically, black-body or cavity radiation would arise from considering the modes (or standing waves) of a conducting cavity. These are solutions to the wave equation for the EM fields subject to suitable boundary conditions at the walls, as discussed last semester. As the fields are vector rather than scalar, the picture is a little more complicated than the solutions to the Schrödinger equation (3.42) but the end result is essentially the same: modes of a cuboidal cavity of sides L_x, L_y and L_z are characterised by the three discrete wave-vector components $\mathbf{k} = (n_x\pi/L_x, n_z\pi/L_y, n_z\pi/L_z)$ with integer n_i. Furthermore for each mode the restriction $\mathbf{k}\cdot\mathbf{E} = 0$ allows for two polarisation states for each $\mathbf{k}$.[6] But classically there is a big difference for EM fields: these are the modes, which are discrete, but the *amplitudes* of the fields of any mode can take any value. We might expect that in thermal equilibrium the energy in each mode would be $k_B T$ (the energy density is quadratic in E and B, so two degrees of freedom). Though the modes are discrete it is an excellent approximation for a macroscopic box to replace the sum with an integral, to give the energy per unit volume in the field for a frequency range $\omega \to \omega + \mathrm{d}\omega$, where $\omega = ck$:

$$u(\omega)\mathrm{d}\omega = k_B T \frac{g(\omega)}{V}\mathrm{d}\omega \qquad \Rightarrow \; u(\omega) = \frac{k_B T}{\pi^2 c^3}\omega^2 \quad ? \tag{4.37}$$

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[6] A nice introduction to cavity modes is given here, but of course it is not examinable.

Experimentally this matches the low-frequency (long-wavelength) spectrum of black-body radiation well and is called the Rayleigh-Jeans law. But clearly it cannot hold for indefinitely large frequency, as it increases without bound: integrating over all frequencies, this would predict that the energy in the EM field of a cavity is infinite, and even the coolest black body would be more than white hot! And indeed, experimentally, deviations are seen at higher frequency: the observed spectrum reaches a maximum and then falls away exponentially. The failure of the Rayleigh-Jeans law has been termed the "ultraviolet catastrophe".[7]

The correct radiation formula was found in 1900 by Max Planck who, in what he described as "an act of desperation", proposed that the amplitude of the fields was not arbitrary, but that the energy in any given mode was quantised, that is it had to be an integer multiple of an elementary energy which is proportional to the frequency—in modern terminology, $E = nhf = n\hbar\omega$. This was the original introduction of h, Planck's constant. Now the single quantum harmonic oscillator is a problem we solved long back, finding (ignoring the zero-point energy)

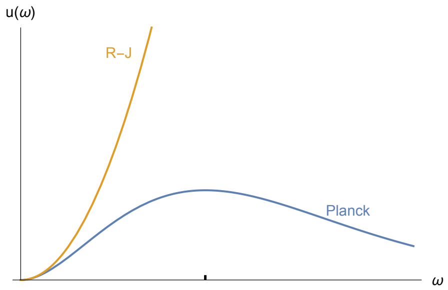
$$\langle E\rangle = \frac{\hbar\omega}{\mathrm{e}^{\hbar\omega\beta} - 1}. \tag{4.38}$$

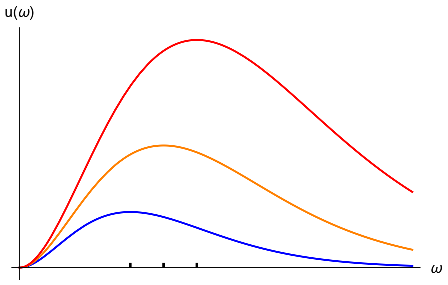
(See (3.37), subtracting $\frac{1}{2}\hbar\omega$.)

Including the density of states to account for the degeneracy at a given ω give the energy per unit volume per unit frequency is

$$u(\omega) = \frac{g(\omega)}{V}\frac{\hbar\omega}{\mathrm{e}^{\hbar\omega\beta} - 1} = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{\mathrm{e}^{\hbar\omega\beta} - 1} \tag{4.39}$$

For low frequencies, $\hbar\omega \ll k_B T$, the denominator can be approximated by $\hbar\omega\beta$ and we recover the Rayleigh-Jeans result (4.37). This is exactly analogous to recovering equipartition for an oscillator. But for high frequencies, the exponential in the denominator dominates and u falls off as $\omega^3\mathrm{e}^{-\hbar\omega\beta}$, curing the ultraviolet catastrophe—and matching experiment nicely with an appropriately-chosen value of the Planck's constant.[8]





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[7] It should be noted that the generally accepted radiation law before Planck was the Wein Law $u \sim \omega^3 \mathrm{e}^{-b\omega/T}$, which in fact is correct at high frequencies. The Rayleigh-Jeans law, though from the start clearly not general, was observed to do better at low energies. The Planck formula we are about to discuss interpolates between the two. As a further interesting note, it was Einstein in 1905 who derived the law together with all the corresponding factors from equipartition, and fully articulated the conflict between this and Planck's law.

[8] Even better, since u depends on $\hbar$ and k_B separately, he could determine both—the latter was not actually known at that point. The gas constant R was, so that immediately gave Avogadro's number N_A. And the product $N_A e$ (the Faraday constant) was also known from electrolysis, so he found e too, all to within a few percent of their currently accepted values, and well before any accurate determination from any other method. Not bad for someone who originally rejected the atomic hypothesis...

The plot above shows, on the left, the Rayleigh-Jeans distribution and the Planck distribution for a given temperature, and on the right, the Planck distribution for three different temperatures. The maximum of the Planck distribution—the frequency with the highest intensity—is at $\omega = 2.82 k_{\scriptscriptstyle B} T/\hbar$, a relation which is called the Wien displacement law. The observation of scaling of the maximum with temperature predates Planck, and is obtained from $\mathrm{d}u/\mathrm{d}\omega = 0$ with the numerical solution of $3(1-\mathrm{e}^{-x}) = x$ at $x = 2.8214$. The sun's surface temperature of 5778 K means that its spectrum peaks in the visible range and its light pretty much defines white. Betelgeuse at 3500 K peaks in the near infrared and appears red, while Sirius at 10000 K peaks in the UV and appears blue.

At this point you might be wondering why we waited till now to cover this application; we could have done it after the ideal gas in section 3. True. But look again at (4.39). In the context of the current section, it should look very familiar: in fact it is just what we expect from an ultrarelativistic Bose gas with chemical potential $\mu = 0$. And indeed we can so interpret it: we can switch from the classical picture of cavity modes of the EM fields with the energy arbitrarily quantised, to a picture of a gas of massless photons of energy $\hbar\omega$. The two polarisation states translate to $g_s = 2$ (unexpected for a spin-1 particle but things work a bit differently when they are massless). Photons, being spin-1, are bosons, so there can be many in any given state. And so the number of photons for a frequency range $\omega \to \omega + \mathrm{d}\omega$, where $\omega = ck$ and $\varepsilon = \hbar\omega$, is

$$\langle N(\varepsilon)\rangle \,\mathrm{d}\varepsilon = g(\varepsilon)\overline{n}(\varepsilon)\mathrm{d}\varepsilon$$

and the energy density is (see the end of section 3.8.1 and the problem sheets for more on changing variables):

$$\begin{aligned} u(\omega)\mathrm{d}\omega &\equiv \frac{\langle E(\varepsilon)\rangle}{V}\mathrm{d}\varepsilon \\ &= \varepsilon\,\frac{g(\varepsilon)}{V}\,\overline{n}(\varepsilon)\,\mathrm{d}\varepsilon = \varepsilon\frac{g_s\varepsilon^2}{2\pi^2(\hbar c)^3}\frac{1}{\mathrm{e}^{\varepsilon\beta}-1}\mathrm{d}\varepsilon \\ &= \frac{\hbar}{\pi^2 c^3}\frac{\omega^3}{\mathrm{e}^{\hbar\omega\beta}-1}\mathrm{d}\omega \end{aligned} \tag{4.40}$$

in agreement with Planck.

Why is the chemical potential for photons zero? The walls of the cavity act as a heat bath but not in any meaningful sense a particle reservoir: photons don't exist in the walls, only energy does. The chemical potential is given by $\mu = (\partial S_{\text{walls}}/\partial N)_E = 0$. This situation occurs where ever particle number is not a conserved quantity.

We should now clarify the relation between cavity and blackbody radiation. Perfect blackbody radiation is obtained as the emission from a small hole in a cavity, and the relation between the two is that the flux $F(\omega)$ of the emitted radiation, that is, the power emitted per unit emitting area, per unit frequency, is related to the energy density in the box by

$$F(\omega) = \frac{c}{4}u(\omega). \tag{4.41}$$

The factor of 4 is the same as enters in the formula for effusion of gas from a small hole. If we integrate over frequency, we get the total flux from an area A of

$$L = \frac{A}{4\pi^2c^2}\int_0^\infty \frac{\hbar\omega^3}{\mathrm{e}^{\hbar\omega\beta}-1}\mathrm{d}\omega = \frac{A(k_{\scriptscriptstyle B}T)^4}{4\pi^2\hbar^3c^2}\int_0^\infty \frac{x^3}{\mathrm{e}^x-1}\mathrm{d}x = \frac{\pi^2 k_{\scriptscriptstyle B}^4}{60\hbar^3c^2}AT^4 \tag{4.42}$$

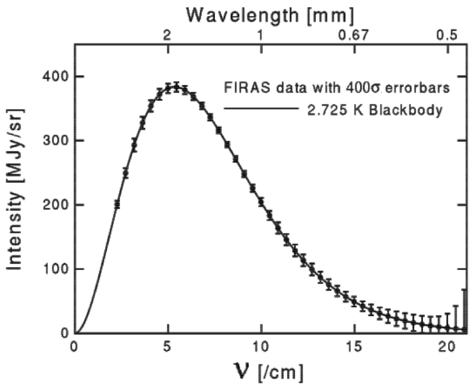
The x-integral has the exact value of $\pi^4/15$.[9]

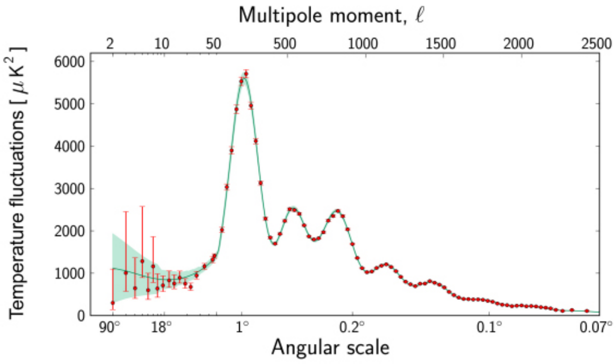
But this is exactly Stefan's law, $L = A\sigma T^4$, except that we have now *predicted* the value of the Stefan-Boltzmann constant σ in terms of Planck and Boltzmann's constants:

$$\sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2}. \tag{4.43}$$

And indeed it does (of course) match with the empirical value.

Stars are not perfect black bodies by any means. The most perfect black body we know is the cosmic microwave background. If you are familiar with cosmology and the results of recent experiments such as WMAP and Planck, you may have a picture like the one below on the right in your head:





But wonderfully informative though that is, it is actually shows the angular scale of deviations, of the order of a few part in 10^5, from a nearly perfect Planck spectrum at a temperature of 2.728 ± 0.004 K. The figure on the left shows the actual spectrum obtained by the FIRAS instrument on the COBE satellite. In the original paper[10] there are no error bars shown because they are "a small fraction of the line thickness"; those in the figure are scaled up by 200 times so they can be seen.

Returning to photons as a bose gas, we can derive some more properties of radiation. The total energy is[11]

$$\langle E\rangle = \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\hbar\omega^3}{e^{\hbar\omega\beta}-1}d\omega = \frac{V(k_BT)^4}{\pi^2(\hbar c)^3}\int_0^\infty \frac{x^3}{e^x-1}dx = \frac{k_B^4\pi^2}{15(\hbar c)^3}VT^4 = \frac{4\sigma}{c}VT^4 \tag{4.44}$$

The grand potential for an ultrarelativistic gas is (see problem sheet 8)

$$\Phi_G = -\tfrac{1}{3}\langle E\rangle\,,$$

so, since $PV = -\Phi_G$,

$$P = \frac{4\sigma}{3c}T^4 \qquad \text{and} \qquad S = -\frac{\partial\Phi_G}{\partial T} = \frac{16\sigma}{3c}VT^3. \tag{4.45}$$

These turn out to be of great importance in cosmology.

In passing we note that for $\mu = 0$, $\Phi_G = F$ and $E = F + TS = TS - PV$.

---

[9] The integral $\int_0^\infty x^3(z^{-1}e^x - 1)^{-1}dx = 6\sum_{n=1}\frac{z^n}{n^4}$, so for $z = 1$ as here we have the sum of the reciprocals of the 4th power of the integers. Those of you doing Complex Variables will have learned a method to sum such series, using the residues of the function $\coth(\pi z)/z^4$.

[10] Fixsen *et al,* Astrophysical Journal **473** (1996) 576; the figure as shown is widely available on the web, attributed to E. L. Wright of UCLA. The right-hand figure is Planck data from ESA.

[11] Many texts use a for $4\sigma/c$. Dr Galla used σ! Don't confuse σ the Stefan-Boltzmann constant with the number density per unit area which often appears on the problem sheets....

4.4.2 Phonons and the Debye model

- **Mandl** 6.3
- **Bowley and Sánchez** 8.7

The switch in perspective from modes of the EM fields in a cavity, to particles—photons—is rather a profound one. Familiarity has perhaps obscured that; most physicists I think would say that photons are “real”. As well as the Planck distribution, processes such as the photoelectric effect and Compton scattering amply attest to the particle nature of light. A similar switch from fields to particles is made for all particles in quantum field theory, in that the theory is formulated in terms of classical-looking fields and then the particles are treated as quantised excitations of these fields. An example you might have heard of is the Higgs: the background field couples to all matter particles giving them mass, but excitations of the field are the short-lived Higgs bosons produced at the LHC. (This is not examinable!)

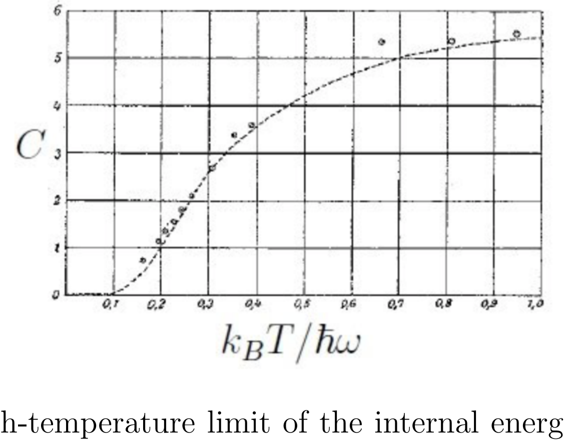
Condensed matter (solid state) physicists deal with complicated systems such as crystals with many excitation modes. Where the energy in these modes is quantised, they also treat the excitations as particles; phonons (from lattice vibrations) are the best known, but magnons (collective excitations of the electrons’ spin), plasmons, rotons (excitations of superfluid ^{4}He) and several more are also discussed. They are known as quasiparticles; they may not be considered “real” but they do exhibit some particle-like behaviours, notably in scattering light and other particles.

In this course we are only, briefly, going to look at phonons.

In the earlier parts of the courses we have repeatedly mentioned Einstein’s model of a crystal, in which every atom vibrates independently with a single frequency ω_E (which can be fit to data): We found (ignoring zero-point energy)

$$\langle E\rangle = N\frac{\hbar\omega_E}{e^{\hbar\omega_E\beta}-1} \qquad\qquad C_V = 3Nk_B\left(\frac{\hbar\omega_E}{k_BT}\right)^2\frac{e^{\hbar\omega_E\beta}}{(e^{\hbar\omega_E\beta}-1)^2} \tag{4.46}$$

The figure below is reproduced from Einstein’s paper Ann. Phys. 22, 180, (1907), with the frequency parameter expressed as a temperature, $\hbar\omega_E/k_B = 1320$ K.



This gives the correct high-temperature limit of the internal energy and heat capacity, but it can be seen to deviate at low temperatures, and indeed is clearly fundamentally flawed. If one atom is displaced, it pulls on its neighbours which will also be displaced, and so on. We are reminded of coupled pendulums; you can set one swinging, but the other will start to swing too. To analyse the subsequent motion we can use the *normal modes* of the whole system, which in this case involve the two pendulums swinging together, either in phase or 180° out of phase; these modes have different frequencies with the in-phase mode being lower that the out-of-phase one. For N pendulums there will be N modes, the lowest-frequency one having all swinging together and the highest frequency one having each out of phase with its neighbour, but with another $N-2$ modes of intermediate frequency. Note that the modes (and hence frequencies) are discrete because the number of pendulums is finite. This is reminiscent of the modes of the EM field in a cavity, which were discrete because the volume was finite, and the allowed wave numbers were multiples of π/L.

For a 1D chain of identical atoms of mass m, with K_s being the effective spring constant between each pair (actually the curvature at the minimum of the interatomic potential), there are two kinds of modes, longitudinal and transverse. For both, the modes are characterised by the distance λ the pattern of atomic displacements to repeat.. The length of the chain sets the maximum λ,[12] and the distance a between the atoms sets the minimum; in terms of wave number, $k = n\pi/L$ for $n = 1, 2 \ldots L/a$. The frequency for longitudinal modes was shown in first year to be $\omega(k) = 2\omega_0 \sin(ka/2)$ where $\omega_0 = \sqrt{K_s/m}$, which at low frequency is $\omega = ka\omega_0$, a linear dispersion relation reminiscent of $\omega = ck$ for photons with $v_s = a\omega_0$ being the speed of sound in the chain. In a simple model, transverse modes have a lower frequency than longitudinal modes of the same k; there are two of these for vibrations in the two planes perpendicular to the direction of the chain.

Introducing quantum mechanics, the energy in each mode will be restricted to multiples of $\hbar\omega$ (again ignoring unobservable zero-point energy), and we see that we have a picture of massless (quasi-)particles corresponding to the excitations in each mode. And either from the quantum oscillator approach of Section 3.7, or by treating the phonons as a bosonic gas with zero chemical potential (same argument as for photons, phonons aren't conserved), we get the number of phonons in a mode as

$$\overline{n}(k) = \frac{1}{e^{\hbar\omega(k)\beta} - 1} \tag{4.47}$$

Even for 3D monatomic crystals with a cubic structure the possible modes of vibration might seem overwhelming. But in fact we can, again, characterise the modes by the wave vector in 3D, $\mathbf{k} = (n_x\pi/L_x, n_y\pi/L_y, n_z\pi/L_z)$ with integer n_i, this time though with a maximum $n_i = L_i/a$. In 3D it is planes of atoms which move together, and $\mathbf{k}$ is parallel to the normal to the plane. The total number of modes is three (for three modes) times the number of ways of choosing n_x, n_y, n_z with each n_i in the allowed range, which is just the product of the three $n_i^{\max}$. So the number of modes is $3L_xL_yL_z/a^3 = 3V/a^3 = 3N$, where N is the number of atoms. That is gratifying, because it is, as it must be, the same as if we treated each atom as vibrating independently in 3D.

This also means that if we are in the high-temperature regime, in which the energy in every mode is k_BT, we will recover the law of Dulong and Petit, $E = 3Nk_BT$ and $C_V = 3Nk_B$, as in the Einstein model.

To find the internal energy and heat capacity due to lattice vibrations at lower temperatures, we would like to use an approach like that for photons, integrating the quantity of interest weighted by $g(k)\overline{n}(k)$, albeit with a cut-off in k. There are some issues with this. Strictly speaking the cut-off on $\mathbf{k}$ is in cartesian coordinates, and furthermore the frequency is not a simple function of $|\mathbf{k}|$, independent of direction. In addition the longitudinal and transverse

---

[12] The existence of a maximum λ of course depends on the boundary condition. If the end atoms are fixed, then $\lambda_{\max} = L/2$. In fact the modes have the end atoms with maximum displacement (cosines rather than sines) and again $\lambda_{\max} = Na/2 = L/2$. If periodic boundary conditions are applied, as is common, $\lambda_{\max} = L$ but there are two modes for each λ and the net effect is the same.

modes do not have the same dispersion relation (wave speed).[13] The Debye model ignores these subtleties, and further assumes a linear dispersion relation $\omega = v_s k$. It imposes a cut-off k_D on $|\mathbf{k}|$ such that the number of modes is correct:

$$3N = \int_0^{k_D} g(k)\mathrm{d}k = \frac{3V}{2\pi^2}\frac{k_D^3}{3} \qquad \Rightarrow \qquad k_D = (6\pi^2 n)^{1/3} \tag{4.48}$$

Then the energy is

$$\langle E\rangle = \int_0^{k_D} \varepsilon(k)g(k)\overline{n}(k)\mathrm{d}k = \frac{3V}{2\pi^2}\hbar v_s \int_0^{k_D} \frac{k^3}{\mathrm{e}^{\hbar v_s k\beta} - 1}\mathrm{d}k \tag{4.49}$$

At very high temperatures, $\beta \to 0$, $\overline{n}(k) \to k_B T/\hbar k v_s$ and we recover $\langle E\rangle = 3Nk_B T$. This is only a consequence of equipartition for each mode and having ensured the correct number of modes, it is does not constitute an independent check of the model.

More generally though, defining $T_D = \hbar v_s k_D/k_B$ (often Θ_D is used instead):

$$\begin{aligned}\langle E\rangle &= \frac{3V}{2\pi^2}\hbar v_s \int_0^{k_D} \frac{k^3}{\mathrm{e}^{\hbar v_s k\beta} - 1}\mathrm{d}k = \frac{3V}{2\pi^2}\hbar v_s \left(\frac{k_B T}{\hbar v_s}\right)^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1}\mathrm{d}x \\ \Rightarrow \quad C_V &= -\frac{3V}{2\pi^2}\hbar v_s \frac{\mathrm{d}\beta}{\mathrm{d}T}\int_0^{k_D} \frac{k^3\,\hbar v_s k\,\mathrm{e}^{\hbar v_s k\beta}}{(\mathrm{e}^{\hbar v_s k\beta} - 1)^2}\mathrm{d}k = \frac{3V}{2\pi^2}k_B \left(\frac{k_B T}{\hbar v_s}\right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\mathrm{d}x \end{aligned} \tag{4.50}$$

For very low temperatures the upper limit on the x integrals in (4.50) becomes large and as the integrand falls off exponentially at large x, we can take the cut-off to infinity. Then the integral in $\langle E\rangle$ is the same as we met in the context of the black body spectrum and equals $\pi^4/15$. So

$$\begin{aligned}\langle E\rangle &\to \frac{V\pi^2}{10}\frac{(k_B T)^4}{(\hbar v_s)^3} \\ \Rightarrow \quad C_V &= k_B V\frac{2\pi^2}{5}\left(\frac{k_B T}{\hbar v_s}\right)^3 = \frac{12\pi^4}{5}k_B N\left(\frac{T}{T_D}\right)^3 \end{aligned} \tag{4.51}$$

Note that the in the first form, the dependence on N has disappeared, which does make sense: only long-wavelength, low frequency modes are contributing; the energy per unit volume only depends on v_s, a bulk property which is insensitive to the atomic substructure. For that reason we expect the result to be reasonably robust, even if some of the model assumptions are somewhat suspect. And so we recover the $C_V \propto T^3$ contribution from lattice vibrations to the specific heat which we saw in the data for potassium in Eq. (4.28). Though T_D can be predicted, it can also be fit to data, as in the figure below on the left, where it can be shown that the different heat capacity curves for a number of metals collapse to a single curve if plotted as a function of T/T_D. (Note: the numbers given for the Debye temperatures are just fit parameters, and other sources using different data will not give identical numbers—see for example Mandl's fig. 6.7.)

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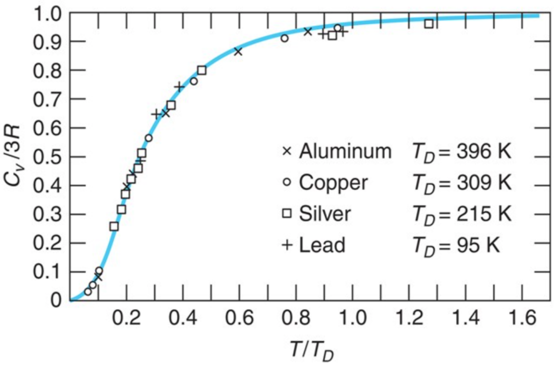
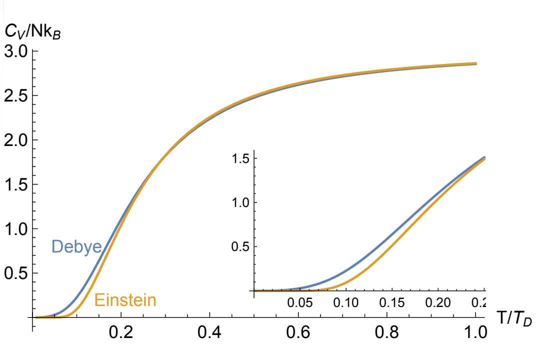
[13] That particular point can be circumvented by using an average speed defined by $3/v_s^3 = 2/v_t^3 + 1/v_l^3$, where v_l and v_t are the speeds of sound for transverse and longitudinal waves respectively; in the expression for the heat capacity (4.50) that is equivalent to calculating the contributions from the two types of modes independently.





The difference between the Debye and Einstein predictions are shown above on the right. Since they both have one free parameter, I have chosen $\omega_E = 0.75\omega_D$ to get the best agreement. Clearly experiment is not going to tell the difference between them except at low temperatures (shown in the inset panel for clarity).

In reality, monatomic simple cubic crystals are not common. However the Debye model works pretty well for more complicated cases too (none of the metals in the figure above are simple cubic). Just for the record, we make a few comments. The density of states in k space, though always derived for a cuboidal box, is independent of the shape of the box. The basic idea that that vibrational modes are *countable* and that a system of N atoms will have $3N$ distinct modes is always valid. The cut-off or maximum value of $\mathbf{k}$ is the edge of the *Brillouin zone*, the set of vectors that cannot be reduced in length by subtracting a reciprocal lattice vector (just as in 1D, a standing wave with wave number $3\pi/4a$ cannot be distinguished from one of $\pi/4a$ because the displacements of the atoms are identical in both). For most structures the Brillouin zone is a polyhedron which is closer to a sphere than the cube is, so that is actually an advantage for the Debye model. Finally for a structure with more than one atom per unit cell (as for any non-monatomic crystal) it is usual to choose the Debye cut-off to reproduce the number of unit cells in the crystal, not the number of atoms. There will be two types of vibration. Three for each $\mathbf{k}$ are like the ones considered above for which $\omega \sim k$ at low frequencies, which are termed acoustic modes and which give the dominant low-temperature heat capacity. The rest are those in which the different types of atom vibrate against each other, termed optical modes (since if the atoms are charged the oscillating dipoles will interact with EM radiation); their frequencies do not go to zero as $k \to 0$. If a crude model is to be used, the constant-frequency Einstein model is more appropriate for these; the correct high-temperature heat capacity will then be recovered. None of these details of real crystals are examinable in this course.

4.4.3 Bose-Einstein condensation

- **Mandl** 11.6
- **Bowley and Sánchez** 10.5

Let us return to matter, and bosons such as ^{4}He and ^{87}Rb, though ignoring any interactions between them (an approximation the validity of which will, broadly, depend on the density—but it should be said at the outset that there are some qualitative changes when interactions are present).

Now for bosons, the occupancy is

$$\overline{n}(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)\beta} - 1} \tag{4.52}$$

and as we have seen, this does not make sense for $\varepsilon < \mu$. So for a Bose gas the chemical potential must be less than the lowest energy level (often taken for convenience to be 0). For a sufficiently warm dilute gas μ will be large and negative and we will be in the classical regime, but as n/n_Q grows, μ will increase (ie become less negative), initially just as in the Fermi case. And as in that case, in practice we find the chemical potential by requiring the density to be correct: for non-relativistic particles in 3D we have

$$\frac{N}{V} = \frac{1}{V}\int_0^\infty g(k)\overline{n}(k)\mathrm{d}k = \frac{g_s}{2\pi^2}\int_0^\infty \frac{k^2}{\mathrm{e}^{(\hbar^2 k^2/2m-\mu)\beta}-1}\mathrm{d}k = \left(\frac{2m}{\hbar^2\beta}\right)^{3/2}\frac{g_s}{4\pi^2}\int_0^\infty \frac{x^{\frac{1}{2}}}{\overline{z}\mathrm{e}^x - 1}\mathrm{d}x \tag{4.53}$$

where as before $\overline{z} = \mathrm{e}^{-\mu\beta}$ and we have made the change of variable

$$x = \frac{\hbar^2\beta}{2m}k^2 \qquad k = \left(\frac{2m}{\hbar^2\beta}\right)^{1/2} x^{1/2}, \qquad \mathrm{d}k = \frac{1}{2}\left(\frac{2m}{\hbar^2\beta}\right)^{1/2} x^{-1/2}\,\mathrm{d}x \tag{4.54}$$

Just as in the finite-temperature Fermi gas, the integral, which can be done numerically, is only a function of $\overline{z}$, which can therefore be adjusted to obtain the correct density.

$$G(\overline{z}) \equiv \int_0^\infty \frac{x^{\frac{1}{2}}}{\overline{z}\mathrm{e}^x - 1}\mathrm{d}x = 4\pi^2 n\left(\frac{\hbar^2}{2mk_{\scriptscriptstyle B}T}\right)^{3/2} = \frac{\sqrt{\pi}}{2}\frac{n}{g_s n_Q}. \tag{4.55}$$

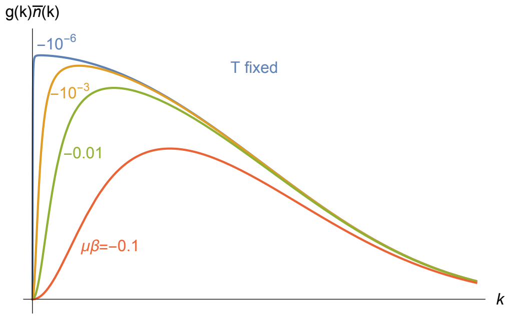
Here, in contrast to the fermion case, $\overline{z} > 1$ always. (Always remember that $n_{\scriptscriptstyle Q} \propto T^{3/2}$.)

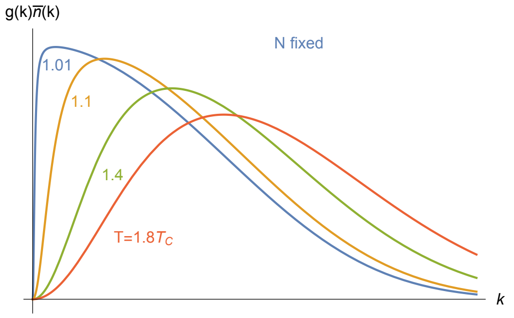
As required, the integral grows as $\overline{z}$ decreases. But it reaches a maximum at $\overline{z} = 1$ ($\mu = 0$) and so there would seem to be a maximum possible value of n/n_Q—for a given density, a minimum temperature! We will return to this, of course. But remaining below this limit on n/n_Q, we obtain the relation between the chemical potential and the number density in the same way as for fermions; the results are shown in green in the second figure of section 4.3.1. (The use of units of $\varepsilon_{\scriptscriptstyle F}$ to eliminate explicit density dependence in that figure is purely a matter of convenience of course, it has no physical meaning for bosons.) The average energy, entropy, pressure and other properties are similarly calculable numerically in terms of integrals like that of (4.55), once the chemical potential is fixed.

Below on the left we show plots of $g(k)\overline{n}(k)$ at fixed temperature for a variety of small (negative) chemical potentials. (We switch to k rather than ϵ because the low-k curve is better behaved.)[14] The area under the curve gives the corresponding N; as expected we see that it grows as falls and μ rises towards zero from below. And as claimed above, the area reaches a maximum as $\mu \to 0$. No more particles can be accommodated.

---

[14] It takes a little thought to convince one's self that $G(\overline{z})$ in (4.55) tends to a finite maximum as $\overline{z} \to 1$, since for $\overline{z} = 1$ the *integrand* diverges as $x^{-1/2}$ for $x \to 0$. But the *integral* does not diverge; it goes as $x^{1/2}$ for $x \to 0$, and so the lower limit contributes zero. (Note $\int_0^a x^{-1/2}\mathrm{d}x = a^{1/2}$). For the full integrand, of course, the upper limit of the integral and hence the final result is finite. Switching to k, at low k we have $g(k)\overline{n}(k) \sim k^2/(\hbar k^2\beta/2m)$ =constant, so the problem does not arise.





On the right we show fixed N for various T (in units of "T_C", here just a shorthand for a quantity that depends on N with units of temperature; defined below in Eq. (4.57)). Again, once $T = T_C$ and $\mu = 0$, no further adjustment can allow the temperature to be lowered further while keeping N fixed.

From all of this, we see that the maximum N or minimum T is obtained when $\mu \to 0$,

$$\begin{aligned}
\frac{N_C}{V} &= \frac{1}{V}\int_0^\infty g(k)\overline{n}(k)\mathrm{d}k = \frac{g_s}{2\pi^2}\int_0^\infty \frac{k^2}{\mathrm{e}^{(\hbar^2k^2/2m)\beta}-1}\mathrm{d}k \\
&= \left(\frac{2m}{\hbar^2\beta}\right)^{3/2}\frac{g_s}{4\pi^2}\int_0^\infty \frac{x^{\frac{1}{2}}}{\mathrm{e}^x-1}\mathrm{d}x = \left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\frac{2.31516\,g_s}{4\pi^2} \\
&= 2.61238\,g_s n_Q
\end{aligned} \tag{4.56}$$

Or in terms of temperature,

$$\boxed{T_C = 3.3125\,\frac{\hbar^2}{mk_B}\left(\frac{n}{g_s}\right)^{2/3}.} \tag{4.57}$$

The subscript C could stand for "critical", though for reasons we will see below it usually stands for "condensation".

But what is going on here? Suppose we just have *one* state, of energy ε. Then for a given μ the occupancy is

$$N = \frac{1}{\mathrm{e}^{(\epsilon-\mu)\beta}-1} \qquad \Rightarrow \qquad \mu = \varepsilon - k_BT\ln\left(1+\frac{1}{N}\right) \approx \varepsilon - \frac{k_BT}{N} \quad \text{for } N \gg 1. \tag{4.58}$$

There is no limit on N! μ just gets closer and closer to ε, from below. So why are we having problems when we allow more than one state (for a particle in a box, using the density of states)?

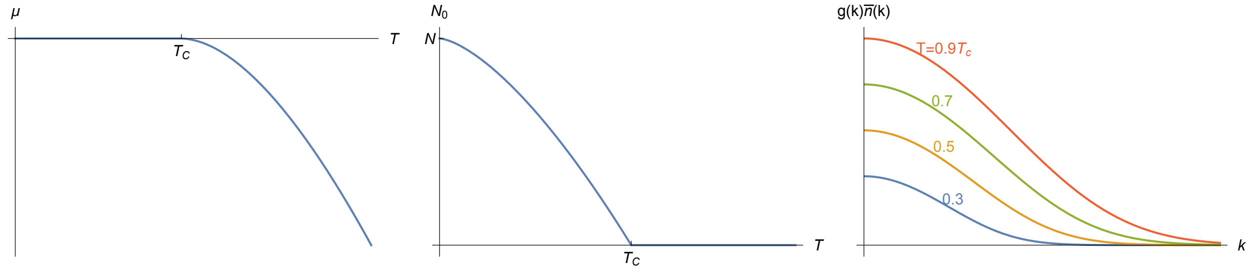
The problem is simply that we have said that everything varies smoothly with k, so that we have replace a sum over discrete states with a weighted integral over k. But as $\mu \to 0$, $\overline{n}(k)$ is varying extremely rapidly at low k. And the weighting, the density of states $g(k) \propto k^2$, vanishes at the lowest energies, so exactly the states we expect to have the most occupancy are given a zero weighting! The apparent limit on n/n_Q, or on T given n, is an artefact of our approximation.

In principle, therefore, we should just switch back to a sum over modes. Recall there is a single ground state, with energy (taking a cube for simplicity) $E_0 = \frac{3\hbar^2\pi^2}{2mV^{2/3}}$, then 3 states with energy $\frac{6\hbar^2\pi^2}{2mV^{2/3}}$, three with $\frac{9\hbar^2\pi^2}{2mV^{2/3}}$ and so on. We can show (it is set as an exercise on the problem sheet) that as we lower the temperature below the critical point, $\overline{n}(\varepsilon)$ continues to vary smoothly over all states except the ground state. So in fact we can continue to use the density of states, so long as we treat the ground state separately:

$$\begin{aligned} N &= N_0 + \int\limits_0^\infty g(k)\overline{n}(k)\mathrm{d}k = N_0 + \frac{g_s V}{2\pi^2}\int\limits_0^\infty \frac{k^2}{\mathrm{e}^{(\hbar^2k^2/2m)\beta}-1}\mathrm{d}k \\ &= N_0 + \left(\frac{2m}{\hbar^2\beta}\right)^{3/2}\frac{Vg_s}{4\pi^2}\int\limits_0^\infty \frac{x^{\frac{1}{2}}}{\mathrm{e}^x-1}\mathrm{d}x \\ &= N_0 + 2.61238\, g_s V n_{\scriptscriptstyle Q} = N_0 + N\left(\frac{T}{T_{\scriptscriptstyle C}}\right)^{3/2} \qquad (4.59) \\ \Rightarrow N_0 &= N\left(1-\left(\frac{T}{T_{\scriptscriptstyle C}}\right)^{3/2}\right). \qquad (4.60) \end{aligned}$$

(where $T_{\scriptscriptstyle C}$ is itself a function of N).

The really important thing to note is that for any T even just a little below $T_{\scriptscriptstyle C}$, N_0 is of the order of N. Maybe a hundredth or a tenth of N, but for macroscopic N that is very much bigger than, say, the fluctuations of order $\sqrt{N}$ that we ignore when using the grand canonical ensemble and applying it to a fixed particle number. As the temperature drops below $T_{\scriptscriptstyle C}$, a macroscopic number of particles "condense" into the ground state: *Bose-Einstein condensation.* This is in comparison with a typical state of higher energy (say $\varepsilon \sim k_{\scriptscriptstyle B}T$) where the occupancy is "a few", of order 1.



As the temperature drops, the fraction of the particles in the condensate rises steadily, till as $T \to 0$, $N_0 \to N$, as shown in the middle panel above. The remainder $(N - N_0)$ corresponds to the the area under the curves in the right hand panel. The condensate is a single, macroscopic, collective quantum object which (for cold trapped atomic gases) can actually be seen by the naked eye.

The energy of the gas is given by

$$\begin{aligned} E &= N\varepsilon_0 + \frac{g_s V}{2\pi^2}\int\limits_0^\infty \frac{k^2\varepsilon(k)}{\mathrm{e}^{(\hbar^2k^2/2m)\beta}-1}\mathrm{d}k \\ &= N\varepsilon_0 + \left(\frac{2m}{\hbar^2}\right)^{3/2}(k_{\scriptscriptstyle B}T)^{5/2}\,\frac{g_s V}{4\pi^2}\int\limits_0^\infty \frac{x^{3/2}}{\mathrm{e}^x-1}\mathrm{d}x \\ \Rightarrow C_{\scriptscriptstyle V} &= k_{\scriptscriptstyle B}\frac{g_s V}{4\pi^2}\left(\frac{5mk_{\scriptscriptstyle B}T}{\hbar^2}\right)^{3/2}\int\limits_0^\infty \frac{x^{3/2}}{\mathrm{e}^x-1}\mathrm{d}x, \qquad (4.61) \end{aligned}$$

where the x integral is just another number. So the heat capacity below T_C is proportional to $T^{3/2}$.[15]

It is also interesting to know what it is just above T_C, because interesting behaviour in the heat capacity is often an experimental sign of a phase transition such as "condensation" in the vapour-liquid context. This is more complicated, because the energy will depend on the non-vanishing μ which is implicitly a function of T. As before writing $\overline{z} = \mathrm{e}^{-\mu\beta}$,

$$E = \left(\frac{2m}{\hbar^2}\right)^{3/2} (k_B T)^{5/2} \frac{g_s V}{4\pi^2} \int_0^\infty \frac{x^{3/2}}{\overline{z}\mathrm{e}^x - 1}\mathrm{d}x$$

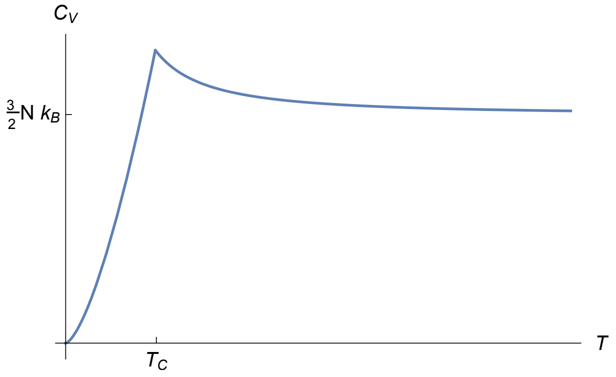
$$\Rightarrow C_V = k_B \left(\frac{5mk_BT}{\hbar^2}\right)^{3/2} \frac{g_s V}{4\pi^2} \int_0^\infty \frac{x^{3/2}}{\overline{z}\mathrm{e}^x - 1}\mathrm{d}x \tag{4.62}$$

$$+ \left(\frac{2m}{\hbar^2}\right)^{3/2} (k_B T)^{5/2} \frac{g_s V}{4\pi^2} \frac{1}{k_B T^2} \left(T\frac{\partial \mu}{\partial T} - \mu\right) \int_0^\infty \frac{\overline{z}x^{3/2}}{(\overline{z}\mathrm{e}^x - 1)^2}\mathrm{d}x \tag{4.63}$$

If we now set $\mu \to 0$, $\overline{z} \to 1$ we get

$$C_V \to k_B \frac{g_s V}{4\pi^2} \left(\frac{2mk_BT}{\hbar^2}\right)^{3/2} \left(\frac{5}{2} \int_0^\infty \frac{x^{3/2}}{\mathrm{e}^x - 1}\mathrm{d}x + \frac{1}{k_B} \frac{\partial \mu}{\partial T} \int_0^\infty \frac{x^{3/2}}{(\mathrm{e}^x - 1)^2}\mathrm{d}x\right) \tag{4.64}$$

The first term is the same as what we found for $T < T_C$, (4.61), so it is continuous. But the second term vanishes below $T = T_C$ and is negative and grows linearly at $T > T_C$. We could go further in the calculation to get an expression for $\frac{\partial \mu}{\partial T}$, but instead we simply plot C_V; it has indeed a cusp at $T = T_C$. This is indicative of a second-order phase transition (like that of the Ising paramagnet).



The relation $P = \frac{2}{3}E/V$ continues to hold below T_C if the contribution of the condensate is ignored, which is a good approximation. But with the vanishing of μ, which above T_C depends on N/V, P depends only on the temperature and not on the volume. This in fact is not physical as the system would not be stable against collapse. But we have ignored interactions; Bose-Einstein gases of real atoms will have repulsive interactions at short distances.

There are a couple of things in the set-up that, on a second reading, might bother you a little. Firstly, the ground state does not have zero energy, so the chemical potential below T_C

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[15] The $N\varepsilon_0$ in E is not a misprint for $N_0\varepsilon_0$. see below.

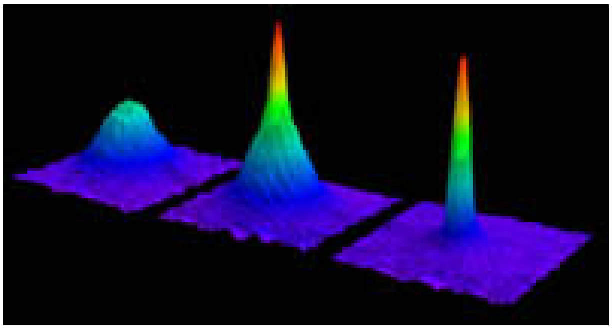
is not actually zero, but given by (from (4.58))

$$\mu = \varepsilon_0 - k_B T \ln\left(1 + \frac{1}{N_0}\right) \approx \varepsilon_0 - \frac{k_B T}{N_0} \tag{4.65}$$

There are two aspects to this: the ε_0 is just a resetting of the zero of energy. In the continuum contribution one likewise shifts the energy so that the variable of integration x is proportional to $\varepsilon - \varepsilon_0$. (It is this shift that makes the first term in the energy in (4.62) up to $N\varepsilon_0$, the zero-point energy of all the particles.) The other aspect is the part that falls as $1/N_0$; for macroscopic occupancy of the ground state that is the part we are truly ignoring when we say $\mu = 0$, and it makes no appreciable difference to the continuum part of the distribution. Second, if the ground state is macroscopically occupied, what about the states just above the ground state? It is true that the continuum approximation may not get their contribution quite right. (It is the continuum *approximation.*) But as you will show on the problem sheet, the occupancy of the first excited state scales as $N^{2/3}$, which for a macroscopic system is many orders of magnitude below N. Only the ground state is macroscopically occupied.

Eric A. Cornell, Wolfgang Ketterle, and Carl E. Wieman received the 2001 Nobel Prize in Physics "for the achievement of Bose-Einstein condensation in dilute gases of alkali atoms, and for early fundamental studies of the properties of the condensates".[16] The JILA paper demonstrated that "a condensate was produced in a vapor of rubidium-87 atoms that was confined by magnetic fields and evaporatively cooled. The condensate fraction first appeared near a temperature of 170 nanokelvin and a number density of 2.5×10^{12} cm^{-3}".[17] The other, from MIT, used ^{23}Na. "The condensates contained up to 5×10^5 atoms at densities exceeding 10^{14} cm^{-3} . The striking signature of Bose condensation was the sudden appearance of a bimodal velocity distribution below the critical temperature of ~ 2 μK. The distribution consisted of an isotropic thermal distribution and an elliptical core attributed to the expansion of a dense condensate."[18]

The famous image below is from the MIT group and shows the velocity distribution above, just below and well below T_C, with the condensate standing out as a spike at zero momentum, distinguished from the more diffuse cloud with a thermal distribution.



Another system of bosons that exhibits interesting behaviour at low temperatures has been known for much longer. ^{4}He liquifies 4.2 K, and never solidifies at normal pressures. At 2.2 K, though, it starts to show very peculiar behaviour, which is known as superfluidity: it behaves as if it had two fluid components, one normal but the other which can flow without viscosity,

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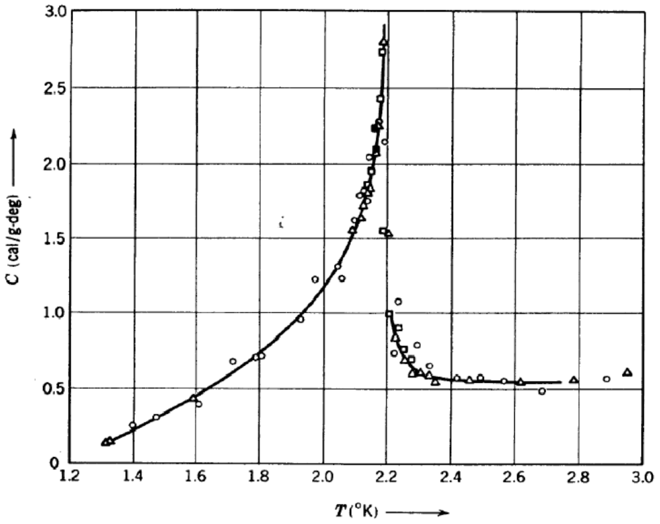
[16] The information accompanying the prize citation is here.

[17] *Observation of Bose-Einstein Condensation in a Dilute Atomic Vapor*, M. H. Anderson, J. R. Enshe, M. R. Matthews, C. E. Wieman, E. A. Cornell, Science (1995) **269** 198.

[18] *Bose-Einstein Condensation in a Gas of Sodium Atoms,* K. B. Davis, M. -O. Mewes, M. R. Andrews, N. J. van Druten, D. S. Durfee, D. M. Kurn, and W. Ketterle Phys. Rev. Lett. **75** (1995) 3969.

which will flow up and over the edge of an open container, and cannot rotate as a bulk fluid. This component is called a superfluid, and as the temperature drops, the superfluid component tends to 100%. At 2.17 K, the heat capacity shows a pronounced spike (see below). ^{3}He, on the other hand, shows no such strange behaviour until the temperature drops to 2 mK. Fritz London in 1938 suggested that the superfluid is in fact a Bose-Einstein condensate; a rough estimate of the BEC transition temperature gives about 3 K, not too far off from the observed one, and if you don't look too closely the heat capacity curve (below) is similar.[19]



In fact non-interacting bosons do not exhibit superfluidity (mathematically that is, they are not experimentally achievable). Dilute cold atom BECs, which are weakly interacting, do show superfluidity, and indeed it has been demonstrated that there is a BEC in liquid ^{4}He. But the condensate fraction never rises above 10%, and it is clear that the interactions (which are strong enough to make it a liquid, after all) are too strong for the treatment we have used to be even an approximate description of the relevant physics.

What about the (fermionic) ^{3}He? How can that show any kind of condensation, even at very low temperatures indeed? In fact this is an example of a phenomenon called *pairing*; if attractive interactions exist then pairs of fermions can form composite bosons (and of course all material bosons are composite); so long as $k_B T$ is well below the binding energy the pairs can form a BEC. Pairing is similarly behind the phenomenon of superconductivity and the superfluidity of the matter of neutron stars. But that is well beyond the scope of this course.

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[19] Figure from F London, *Superfluidity*, Wiley 1954. In fact the helium heat capacity diverges, albeit only logarithmically, at the critical temperature.

Appendix A

Miscellaneous background

A.1 Revision of ideal gas

Just as important as knowing these equations is knowing that they **only** apply to ideal gases!

An “ideal” gas is one with point-like, non-interacting molecules. However the molecules are allowed to be poly-atomic, and so have internal degrees of freedom (rotational, vibrational). The behaviour of all gases tends to that of an ideal gas at low enough pressures; at STP noble gases such as argon are very close to ideal, and even air is reasonably approximated as ideal.

Ideal gases obey the ideal gas law

$$PV = nRT \qquad \text{or} \qquad PV = Nk_B T \tag{A.1}$$

where N is the number of molecules, $n = N/N_A$ is the number of moles (not to be confused with the number density, N/V, also denoted by n), $R = 8.314\,\mathrm{JK^{-1}}$ and $k_B = R/N_A = 1.381 \times 10^{-23}\,\mathrm{JK^{-1}}$ is Boltzmann’s constant. The ideal gas law encompasses Boyle’s Law and Charles’ Law. It requires the temperature to be measured on an absolute scale like Kelvin’s.

Ideal gases have internal energies which depend only on temperature: if C_V is the heat capacity at constant volume,

$$\begin{aligned} E = E(T) \qquad \text{and} \qquad \mathrm{d}E &= C_V \mathrm{d}T \\ \Rightarrow E &= C_V T \qquad \text{if } C_V \text{ is constant} \end{aligned} \tag{A.2}$$

In general the heat capacity may change with temperature; however at STP it is usually adequate to consider it as constant and equal to

$$E = \tfrac{1}{2} n_f R \tag{A.3}$$

per mole, where n_f is the number of active degrees of freedom. For monatomic gases $n_f = 3$ (translational) and for diatomic gases $n_f = 5$ (translational and rotational; vibrational modes are “frozen out”.)

The heat capacities at constant pressure and at constant volume differ by a constant for ideal gases:

$$C_P - C_V = nR. \tag{A.4}$$

During reversible adiabatic compression or expansion of an ideal gas the pressure and volume change together in such a way that

$$PV^{\gamma} = \text{constant} \qquad \text{where} \qquad \gamma \equiv \frac{C_P}{C_V} \tag{A.5}$$

For a monatomic gas at STP, $\gamma = 5/3 = 1.67$; for a diatomic gas, $\gamma = 7/5 = 1.4$. Using the ideal gas law, we also have

$$TV^{\gamma-1} = \text{constant} \qquad \text{and} \qquad TP^{\frac{1}{\gamma}-1} = \text{constant}. \tag{A.6}$$

Note that $\gamma - 1 = nR/C_V$.

Starting from the fundamental thermodynamic relation 1.11 together with the equation of state A.1 and energy-temperature relation ig:energy, we can show that the entropy change of a n moles of moles of ideal gas

$$\Delta S = nR \ln \left(\left(\frac{T_f}{T_i} \right)^{n_f/2} \frac{V_f}{V_i} \right) \tag{A.7}$$

Since $\mathrm{d}S = \frac{C_v}{T}\mathrm{d}T$ at constant volume, this can be checked experimentally for any gas which is close enough to ideal. But as the expression is ill-defined as $T_i \to 0$, classical thermodynamics cannot predict the absolute entropy even of an ideal gas.

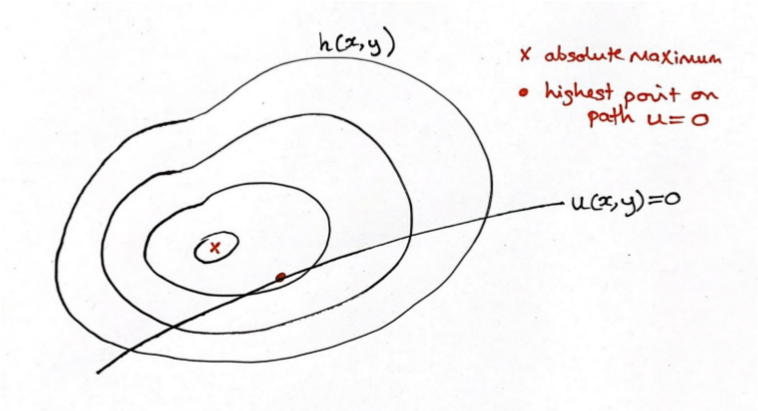
A.2 Lagrange multipliers for constrained minimisation

Arfken 22.3
Riley 5.9

Consider a hill with height $h(x, y)$ (atypically, here, we use y as an independent variable). To find the highest point, we want to simultaneously satisfy

$$\frac{\partial h}{\partial x} = 0 \qquad \text{and} \qquad \frac{\partial h}{\partial y} = 0 \tag{A.8}$$

(checking that it really is a maximum that we've found). But consider a different problem: on a particular path across the hill (which does not necessarily reach the summit) what is the highest point reached? The path may be specified as $y = g(x)$ or more symmetrically as $u(x, y) = 0$. This is *constrained maximisation*: we are constrained to stay on the path.



The trick is to extremize $h(x,y)+\lambda u(x,y)$ with respect to x and y; these two equations together with the constraint $u(x,y)=0$ are enough to fix the three unknowns x_m, y_m and λ (though the value of the last is uninteresting and not usually found explicitly; this is also called the method of "undetermined multipliers".) So for example with a hemispherical hill $h=h_0(1-x^2-y^2)$ and a straight-line path $u(x,y)=y-mx-c=0$ we have[1]

$$\begin{aligned}\frac{\partial(h+\lambda u)}{\partial x}=0 \quad &\Rightarrow -2h_0x-\lambda m=0 \quad &&\Rightarrow x=-\lambda m/2h_0\\ \frac{\partial(h+\lambda u)}{\partial y}=0 \quad &\Rightarrow -2h_0y+\lambda=0 \quad &&\Rightarrow y=\lambda/2h_0=-x/m.\end{aligned} \tag{A.9}$$

Combining the constraint $y-mx-c=0$ with $y=-x/m$ gives $x=-c/(m^{-1}+m)$, so the maximum is reached at

$$(x_m,y_m)=\frac{c}{1+m^2}(-m,1), \qquad h_m=h_0\frac{1+m^2-c^2}{1+m^2}. \tag{A.10}$$

As promised we didn't find λ, though we could. In this case we could simply have substituted $y=mx+c$ into $h(x,y)$ and minimised with respect to x alone, which would have been easier (check!), but for a more complicated hill and/or path Lagrange's method is simpler.

A.3 Hyperbolic Trigonometry

Remember that ordinary trig functions are defined as follows:

$$\cos\theta=\frac{1}{2}(e^{i\theta}+e^{-i\theta}) \qquad \sin\theta=\frac{1}{2i}(e^{i\theta}-e^{-i\theta}) \tag{A.11}$$

and it is useful sometimes to use the extra functions

$$\sec\theta\equiv\frac{1}{\cos\theta} \qquad \operatorname{cosec}\theta\equiv\frac{1}{\sin\theta} \qquad \cot\theta\equiv\frac{1}{\tan\theta} \tag{A.12}$$

Hyperbolic trig functions are defined similarly:

$$\cosh x=\tfrac{1}{2}(e^{x}+e^{-x}) \qquad \sinh x=\frac{1}{2}(e^{x}-e^{-x}) \tag{A.13}$$

$$\operatorname{sech}x\equiv\frac{1}{\cosh x} \qquad \operatorname{cosech}x\equiv\frac{1}{\sinh x} \qquad \coth x\equiv\frac{1}{\tanh x} \tag{A.14}$$

From the definitions above it is easy to show that

$$\frac{\mathrm{d}\cosh x}{\mathrm{d}x}=\sinh x \qquad \frac{\mathrm{d}\sinh x}{\mathrm{d}x}=\cosh x \qquad \frac{\mathrm{d}\tanh x}{\mathrm{d}x}=\operatorname{sech}^2 x. \tag{A.15}$$

Often we are interested in the small- or large-x limits of these functions. What we want is to find a simple function which approximates to a more complicated one in these limits. So while it is true that as $x\to 0$, $\sinh x\to 0$, that is not usually what we want; what we want is *how* it tends to zero.

---

[1] Some presentations of this subject add the equation $\frac{\partial(h+\lambda u)}{\partial\lambda}=0$ to the list, but from that we just recover the imposed constraint $u=0$.

From the small-x expansion of the exponential $e^x = 1 + x + \frac{1}{2}x^2 + \ldots$ we get

$$\sinh x \xrightarrow{x\to 0} x \qquad \tanh x \xrightarrow{x\to 0} x \qquad \cosh x \xrightarrow{x\to 0} 1 + \tfrac{1}{2}x^2 \tag{A.16}$$

The limit of $\cosh x$ often causes problems; whether we keep the x^2 term depends on the context, given that we want to be able to say more than "tends to 0" or "tends to ∞". It may be useful to remember instead

$$\cosh x \xrightarrow{x\to 0} 1 \qquad \text{but} \qquad \cosh x - 1 \xrightarrow{x\to 0} \tfrac{1}{2}x^2 \tag{A.17}$$

The same is true of the exponential:

$$e^x \xrightarrow{x\to 0} 1 \qquad \text{but} \qquad e^x - 1 \xrightarrow{x\to 0} x. \tag{A.18}$$

In a particular problem we find that the energy of a system is

$$\langle E\rangle = \frac{\hbar\omega}{e^{\hbar\omega\beta} - 1} \tag{A.19}$$

Naively we would say that at high temperatures, as $\beta \to 0$, the denominator vanishes and the energy tends to infinity. That is true but not very helpful. If we are more sophisticated we see that the denominator actually tends to $\hbar\omega\beta$ and $\langle E\rangle \to 1/\beta = k_B T$. That is a much more useful prediction, since it can be verified experimentally.

The high-x limits are easier; $e^{-x} \to 0$ and so

$$\sinh x \xrightarrow{x\to\infty} \tfrac{1}{2}e^x \qquad \cosh x \xrightarrow{x\to\infty} \tfrac{1}{2}e^x \qquad \tanh x \xrightarrow{x\to\infty} 1 \tag{A.20}$$