

PC2352 Thermal and Statistical Physics

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Course details and how to use these notes

These lecture notes are intended for students studying PC235 Thermal and Statistical Physics. They are not a substitute for lectures, nor for text books, but are intended to help understand the most important ideas.

Important equations are displayed in yellow boxes.

But note that not every equation is universally true, so be sure to understand the context.

The text has lots of hypertext links. Some link back to previous sections to remind you of results and definitions which are about to be used; others link to examples or help with maths, and still others link to details of derivations. Don't over-use these links, especially of the first kind, or you will easily lose the thread of the argument. It is good practice to read a section through before exploring any of the links, and then ask yourself what you hope to find before exploring a link. That said, don't skip the examples!

Other sources

The recommended texts for the course are

Mandl, F. *Statistical Physics* 2nd edition (Wiley)

Bowley, R. and Sanchez, M. *Introductory Statistical Mechanics* (Oxford)

For the thermal section of the course, there is also

Adkins, C. J. *Equilibrium Thermodynamics* 2nd edition (McGraw Hill)

Zemansky, M. W. and Dittman, R. H. *Heat and Thermodynamics* 7th edition (McGraw Hill)

and for the statistical sections,

Kittel, C. and Kroemer, H. *Thermal Physics* 2nd Edition (Freeman)

Here are some links to external sites on statistical thermodynamics. (I'll check them occasionally, but I apologise in advance for broken links!)

An almost entirely non-mathematical introduction to the subject by T. W. Leland is [here](#). If you find the current site lacking in words, you might like it. Note that "correct" on the penultimate line of the last page should read incorrect!

Various other UK universities run courses like this and have material available on the web. The closest to ours seems to be [PHYS-213](#) at Keele. They use Mandl as a textbook too.

At Leeds it's a third year course, [PHYS 3370](#). The main difference from ours is that they tackle isolated systems with fixed energy directly, via Lagrange multipliers, rather than indirectly via systems in contact with a heat bath (see remarks at the start of the section [Statistical Physics of Non-isolated Systems](#)). With that proviso, though, it could be useful. Note they use “localised systems” to mean those, like the paramagnet, with distinguishable particles, and “non-localised systems” to mean those, like the ideal gas, with indistinguishable particles.

An interesting “timeline” history of ideas in statistical physics can be found [here](#), courtesy of Jeff Biggus, formerly of the University of Colorado, USA

Disclaimer

These notes are available from outside the department at the following URL:
External users are welcome to browse them, and I'd be happy to hear your comments. However please be aware that these are in no way a substitute for a textbook (the closest, and the one which I have used heavily in preparing the course, is Mandl), and many subtleties are glossed over or totally ignored!

There are bound to be many misprints in these pages, and small rewards are available to Manchester students who point them out! Click [here](#) to mail me.

Chapter 1

Classical Thermodynamics: the first law

In this section we revise the concepts of heat, work and internal energy. You should check that you remember the properties of an ideal gas, summarised without proof [here](#). You should also check out the [glossary](#) for the meaning of terms like “adiabatic” and “function of state” which will be assumed.

The only new material in this section is the [definition of work](#) in systems other than hydrostatic. However if past years are anything to go by, it is unlikely you will remember much of it without revision.

1.1 The First Law of Thermodynamics

Take-home message: The sum of the work done on and the heat added to a system is a function of state. It is called the internal energy.

For [adiabatic](#) changes the amount of **work** required to produce a given change of state is independent of the way the work is done. This suggests that the internal energy E of the system is a [function of state](#).

For non-adiabatic changes energy can also enter or leave the system as **heat**, and the work done is no longer independent of the process. However the sum of energy added in the form of heat and work is. This is the **first law of thermodynamics**:

$$\Delta E = Q + W$$

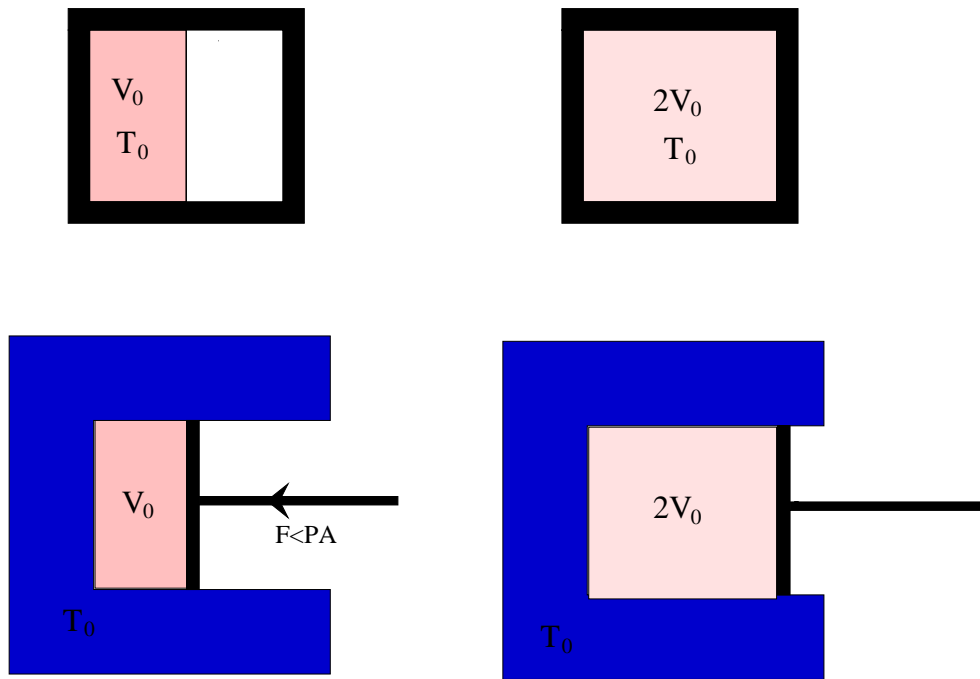
Remember Q is the heat added **to** the system and W is the work done **on** the system (eg by compression). (Warning: if you surf the web you will come across sites written by chemists, and they use a different sign convention.)

Mancunian [James Joule](#) was a key figure in establishing the interconvertability of work and heat.

Here we have an example of two different processes which involve the *same* change in state. We start with an ideal gas at (V_0, T_0) and in both cases the final state is $(2V_0, T_0)$.

In the first case the gas is initially confined to one half of an insulated container. When the partition is removed it fills the whole container. Here no heat is exchanged or work done, so

$$\Delta E = 0$$



Because the gas is ideal, [the energy is a function of temperature only](#), so no change in internal energy means no change in temperature.

In the second case the temperature is held constant by a heat bath. The expansion does work against an external force, so $W < 0$. However the endpoint is *the same* as in the previous case, so once again $\Delta E = 0$. Thus there must be a flow of heat into the system:

$$Q = \Delta E - W = |W|$$

References

- Mandl 1.3
- Bowley and Sánchez 1.5
- Adkins 3.1-4
- Zemansky 4.1-6

1.1.1 James Joule

James Joule - Mancunian (born Salford 1818, died Sale 1889), brewer and Physicist

Experiments like the one above around 1845 helped to establish the 1st law beyond reasonable doubt. The temperature of the system can be raised either by doing Mgh of mechanical work on it or by adding $C\Delta T$ of heat (where h is the distance through which the weight falls and C is the heat capacity of the fluid). Afterwards there is no way of deducing which method was used to increase the internal energy.

A photo of actual apparatus used by Joule can be found [here](#), courtesy of the Science Museum in London. The text of one of his papers is [here](#). In it he speculates about the temperature increase of water in a waterfall. During his honeymoon in the Alps in 1849 he attempted to verify his speculations, but inconclusively. Mrs Joule's reactions are not recorded. More about Joule [here](#) ©"Zephyrus".



1.2 The First Law for Small Changes

Take-home message: Heat and work are not functions of state

In mathematics, if f is a function, df is the notation used for an infinitesimal change in f . Internal energy is a function (of the other state variables) so we can use dE for the change in E between two nearly identical states. During this infinitesimal change, tiny amounts of heat have been added to, and work done on, the system. These are not **changes** in anything, though, so we use a different notation for them, δQ and δW :

$$dE = \delta Q + \delta W$$

Finite changes in state variables are written with a Δ , but finite amounts of heat and work are just written Q and W , as in $\Delta E = Q + W$

[More on notation here.](#)

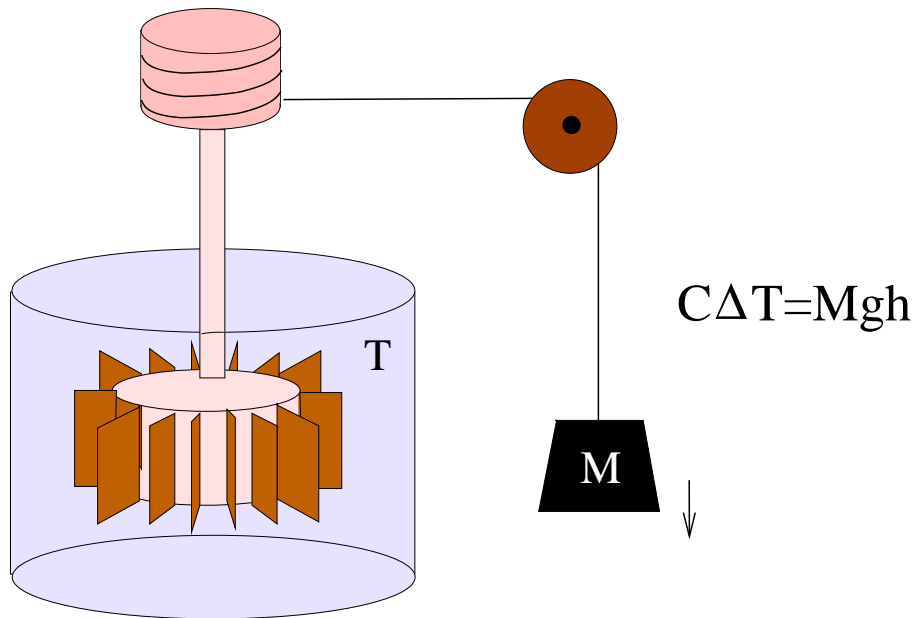
References

- Mandl 1.3
- Bowley and Sánchez 1.5
- Adkins 3.4
- Zemansky 4.6

1.2.1 Notation for finite and infinitesimal changes

After marking last year's exam, I realised that some students have a problem with the manipulation of finite and infinitesimal changes. I hope the following helps.

If we are dealing with functions of state, there are three ways they could enter:



- As **totals**, for instance in the following expressions for a classical ideal gas

$$PV = nRT; \quad E = \frac{3}{2}nRT; \quad S = nR \left(\ln V + \frac{3}{2} \ln E \right) + S_0.$$

- As **differentials**, for instance in the fundamental thermodynamic relation,

$$dE = TdS - PdV$$

- As **finite changes**, for instance for a process at constant volume with a heat capacity which is independent of temperature

$$\Delta S \equiv S_2 - S_1 = C \ln \frac{T_2}{T_1}$$

There are two basic rules:

- If one term in an equation involves an infinitesimal, all the other terms must also contain one (and only one!).
- If finite changes are involved, all terms will have reference to the initial and final states.

Introducing things like heat and work which aren't functions of state complicates things slightly; the first rule still holds (though we write dQ and dW). However **changes** in functions of state can be related to **amounts** of heat and work, as in $\Delta E = Q + W$.

Another common mistake is to assume that if something involving a differential holds, the same relation will hold for finite changes. This is not generally true. For instance for an *isothermal* expansion of an ideal gas E is constant, so

$$TdS = PdV \quad \text{and} \quad T\Delta S = \int_{V_1}^{V_2} PdV \quad \text{but} \quad T\Delta S \neq P\Delta V.$$

Why not? Well T **is** constant so TdS **can** be integrated to $T\Delta S$, but P certainly isn't constant so $\int PdV \neq P \int dV$. What we can do here is substitute $P = nRT/V$, giving $T\Delta S = nR \ln(V_2/V_1)$.

Similarly,

$$dS = \frac{dQ^{\text{rev}}}{T} \not\Rightarrow \Delta S = \frac{Q^{\text{rev}}}{T}$$

unless T is constant. However if the heat capacity is constant, as is a reasonably good approximation for most solids and gases at STP, we can write $dQ = CdT$ and integrate to get $\Delta S = C \ln(T_2/T_1)$.

1.3 Cycles

Take-home message: If a process returns a system to its starting point, all functions of state are unchanged, but net heat may be added to the system, and work done by it.

By definition, functions of state return to their starting value at the end of a cycle. However heat and work are not functions of state, so

$$\oint dE = 0 = \oint dQ + \oint dW$$

and

$$\oint dQ = - \oint dW$$

but in general

$$\oint dQ \neq 0 \quad \text{and} \quad \oint dW \neq 0$$

(Note that \oint is used for the integral round a cycle.)

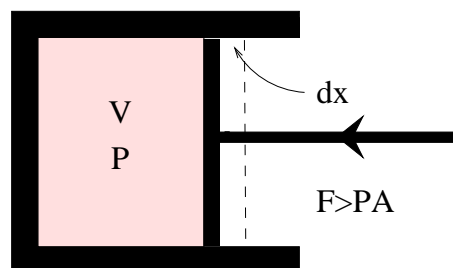
References

- Mandl 1.3

1.4 Work

Take home-message: the expressions for reversible work for various systems

First, we consider the work done in compressing a fluid (hydrodynamic system).



In any real case, compression requires the applied force to be greater than the internal pressure times the area of the piston: $F > PA$. The work done in moving the piston through dx is

$$dW = Fdx = -\frac{F}{A} dV > -P dV$$

Note this is **positive** for compression, because dV is negative.

If there is no friction, and the compression is done extremely slowly, the applied force will only be barely greater than PA . In that case the process is **reversible**, and the inequality will become an equality:

$$dW^{\text{rev}} = -P dV$$

See [here](#) to revisit a previous example.

Similarly to reversibly stretch a wire of tension Γ (that's a capital gamma) by dl requires

$$dW^{\text{rev}} = \Gamma dl$$

and to increase the area of a film of surface tension γ by dA requires

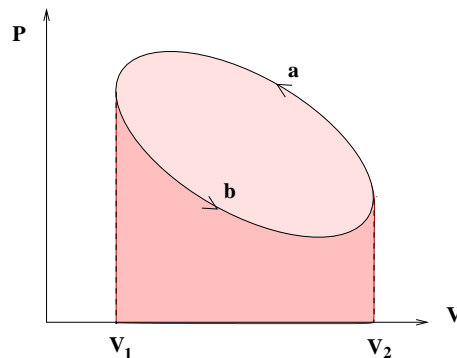
$$dW^{\text{rev}} = \gamma dA$$

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 (dl or dA positive) but to *compress* a gas (dV negative).

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

$$dW^{\text{rev}} = -\mathbf{m} \cdot d\mathbf{B} = -V\mathbf{M} \cdot d\mathbf{B}$$

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



If reversible processes are represented by lines on a plot of pressure against volume (or tension against length, or...), then the magnitude of the work done is equal to the area under the line. Cycles are closed loops as in the picture above, and the magnitude of the work done is equal to the area of the loop (that is, the difference between the areas under the two lines).

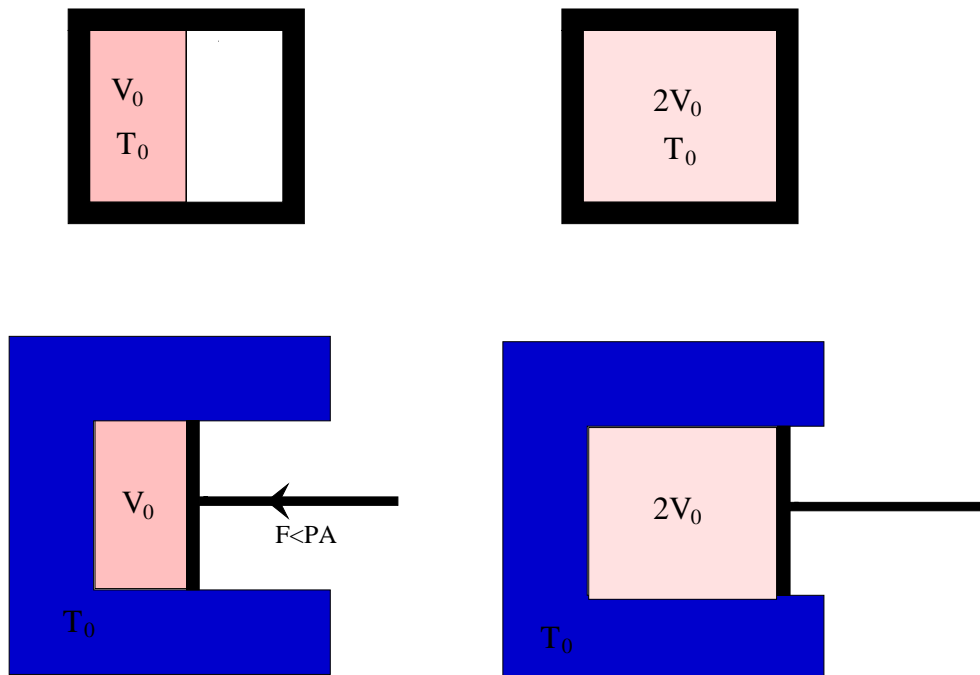
Test yourself with this [example](#). More can be found on the tutorial sheet.

References

- Mandl 1.3-4
- Bowley and Sánchez 1.6
- Adkins 3.5
- Zemansky 3

(Be warned: Adkins and Zemansky use a different definition of magnetic work, which is less convenient for statistical thermodynamics.)

1.4.1 Work during free and reversible expansions

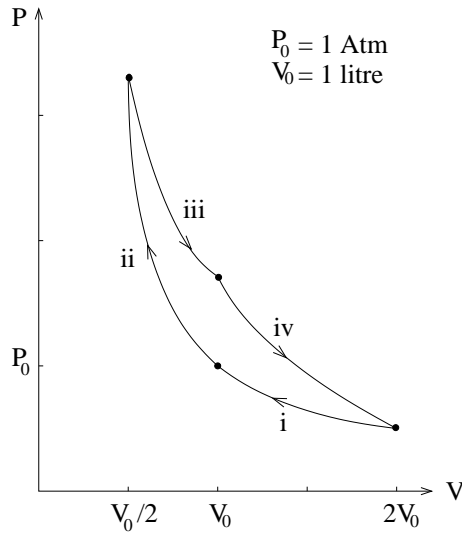


In this example (see [here](#)) we saw that the work done **by** an ideal gas during **isothermal expansion** could be zero (for free expansion into a vacuum) or non-zero (for expansion against a force). In the first case the process is non-reversible. We now see that in the second case, if the process is reversible, the work done *by* the gas *on* the surroundings will be

$$-W^{\text{rev}} = \int P dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}$$

where we used the [ideal gas law](#) $P = nRT/V$, and we could take T out of the integral because the process is isothermal.

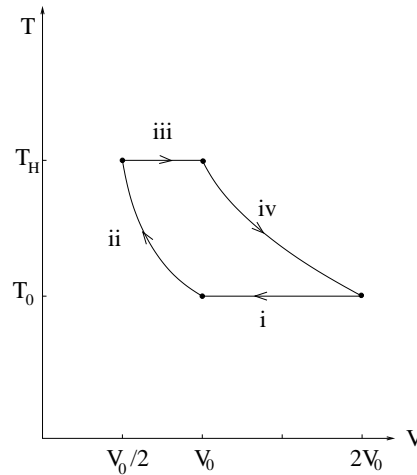
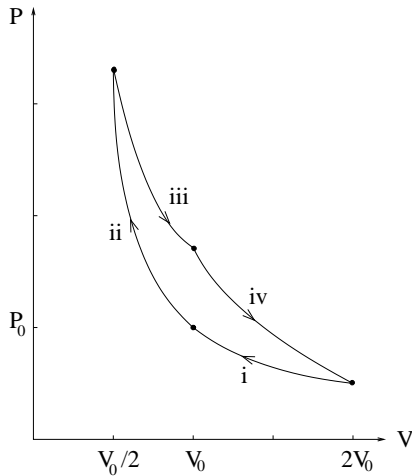
The reversible process extracts the maximum work from the gas, as no work is lost overcoming friction or creating sound waves. In a non-reversible process, these are both mechanisms which convert energy which could have gone into work into internal energy of the gas instead, and so the gas will need to extract less heat from the surroundings. Thus $Q + W = 0$ will still hold.



1.4.2 Example of calculation of work

In this cycle the system, which is an ideal monatomic gas, undergoes first isothermal (i) then adiabatic (ii) compression steps, each of which halve the volume, then returns to its starting point via first isothermal (iii) and then adiabatic (iv) expansions, each of which double the volume. How much work is done by the system during the cycle if P_0 is 1 atmosphere and $V_0 = 1$ litre?

The short answer is 41.3 J. [The full answer is here.](#)



Answer Above we see the cycle plotted both on a $P-V$ and $T-V$ plot. Note that P_0 and V_0 are the pressure and volume at the end of the first step, not at the beginning!

We have [already calculated](#) the work done on the gas during an isothermal volume change:

$$W^{\text{isoth}} = -nRT_1 \ln(V_2/V_1)$$

For the adiabatic stages we use $PV^\gamma = \text{const}$ (see properties of an [ideal gas](#)) to get

$$W^{\text{adiab}} = -P_1 V_1^\gamma \int_{V_1}^{V_2} \frac{1}{V^\gamma} dV = \frac{P_1 V_1}{\gamma - 1} \left[\left(\frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right] = \frac{nRT_1}{\gamma - 1} \left[\left(\frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right] = c_V(T_2 - T_1)$$

(Note that $nR/(\gamma - 1) = c_V$! Can you think of an easier way of obtaining this expression for the work? Hint: no heat is exchanged, so $W = \Delta E$.)

All we need is the temperature of the isothermal expansion, which is also the temperature at the end of the adiabatic compression. Using $TV^{\gamma-1} = \text{const}$ gives $T_2 = T_1(V_1/V_2)^{\gamma-1}$ so $T_H = 2^{\gamma-1}T_0$ where $T_0 = P_0V_0/nR$.

So

$$\begin{aligned} W^{(i)} &= -nRT_0 \ln(1/2) = nRT_0 \ln 2 \\ W^{(ii)} &= c_V(T_H - T_0) \\ W^{(iii)} &= -nRT_H \ln 2 \\ W^{(iv)} &= c_V(T_0 - T_H) \\ W^{\text{tot}} &= nR \ln 2(T_0 - T_H) = -P_0V_0 \ln 2 (2^{\gamma-1} - 1) \end{aligned}$$

The work done **by** the system is minus this; using $\gamma = 5/3$ for a monatomic gas we get 0.407 atmosphere-litres or 41.3 J.

The work done during the adiabatic steps (ii) and (iv) cancels. We could have guessed this, as the work done by the system during the cycle must equal the net heat absorbed. Heat is only absorbed or given out in the isothermal steps, and its magnitude is equal and opposite to the work done on the system in those steps. So we could more simply have written $W^{\text{tot}} = -(Q^{(i)} + Q^{(iii)}) = W^{(i)} + W^{(iii)}$.

1.5 Temperature

Take-home message: Systems have a property, temperature, which is the same for two systems in thermal equilibrium

Two bodies are in **thermal equilibrium** if no heat flow occurs when they are brought into contact. This is an extension of the idea of equilibrium for a single system, when no net internal heat flow occurs.

The **Zeroth law of thermodynamics** says that if two bodies are separately in thermal equilibrium with a third body, they are also in thermal equilibria 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** temperature scale, measured in Kelvin and defined to be 273.16 K at the triple point of water:

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

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.

A nice elementary site on the history of temperature from the US National Center for Atmospheric Research can be found [here](#).

Off-line, Adkins and Zemansky each devote a whole chapter to the subject.

References

- (Mandl 1.2)
- Bowley and Sánchez 1.2
- Adkins 2
- Zemansky 1

Chapter 2

Classical Thermodynamics: The second law

In this section, we start from the experimental fact that heat engines are never 100% efficient, and also that there is a natural direction to spontaneous processes (such as the cooling of a cup of coffee), and derive the existence of a new function of state, **entropy**.

In classical thermodynamics, entropy “completes the set” of relevant thermodynamic variables and, starting with the **fundamental thermodynamic relation** and using **Maxwell’s relations**, enables us to work out what is happening to systems during a variety of processes.

The underlying meaning of entropy however is only clarified when we progress to **statistical physics**.

(Some of the early part of this section will be revision, but the overall approach to entropy is new.)

2.1 Heat Engines and Refrigerators

Take-home message: The production of work from heat requires a temperature gradient. It is an inefficient process—most of the energy is lost as waste heat

In any heat engine, heat is extracted from a hot source (eg hot combustion products in a car engine). The engine does work on its surroundings and waste heat is rejected to a cool reservoir (such as the outside air). It is an experimental fact that the waste heat cannot be eliminated, however desirable that might be. Indeed in practical engines, more of the energy extracted from the hot source is wasted than is converted into work.

The **efficiency** η of a heat engine is the ratio of the work done W to the heat extracted from the hot source Q_H :

$$\eta_{\text{engine}} = \frac{W}{Q_H}$$

If Q_C is the rejected heat, we have by conservation of energy

$$Q_H - Q_C = W$$

More details on heat engines can be found [here](#).

An example of an efficiency calculation for a particular cycle (the Otto cycle) can be found [here](#).

Heat engines can also be used to pump heat from colder to hotter bodies. This always needs an input of work. Examples are fridges, air conditioners and heat pumps. These are all

essentially the same, but the in the first two the purpose is to cool (or keep cool) a fridge, room or building and in the last, the purpose is to heat (or keep hot) a building. In these cases what we call the efficiency is different. In general

$$\text{efficiency} = \frac{\text{desired output}}{\text{costly input}}$$

In the heat engine, it is Q_H that is costly (eg, petrol!) and W that we want out, so as already given,

$$\eta_{\text{engine}} = \frac{W}{Q_H} < 1 \quad \text{always}$$

In the fridge or air conditioner, it is the work that is costly (electricity) and the desired result is the extraction of Q_C from the room or fridge, so

$$\eta_{\text{fridge}} = \frac{Q_C}{W} > 1 \quad \text{usually}$$

In the heat pump, it is again the work that is costly (electricity) and the desired result is the addition of Q_H to the building, so

$$\eta_{\text{pump}} = \frac{Q_H}{W} > 1 \quad \text{always}$$

These are sometimes called “coefficients of thermal performance” because students are worried by “efficiencies” greater than one. There would be no point in the heat pump if its efficiency, as we’ve defined it, were less than one—we’d just use an electric heater (efficiency exactly one) instead!

Note that real engines are optimized to perform forward or backwards, and are not **reversible** in the technical sense (there is friction, processes are not quasistatic). Thus relative sizes of W , Q_H and Q_C will depend on the direction. However for idealized, reversible engines only the signs will change, and we have

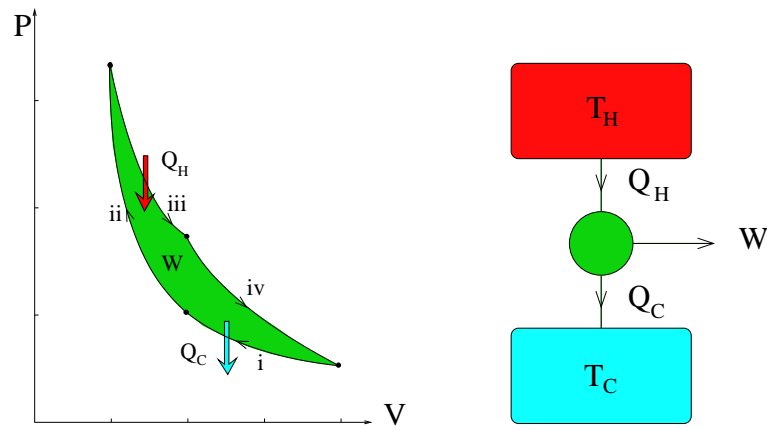
$$\eta_{\text{pump}}^{\text{rev}} = \frac{1}{\eta_{\text{engine}}^{\text{rev}}}$$

Often we are concerned with engines operating between only two reservoirs - one hot and one cold. In that case there is a standard way of denoting a heat engine, given below with the corresponding cycle in the $P - V$ plot. If all the arrows are reversed it represents a heat pump or fridge.

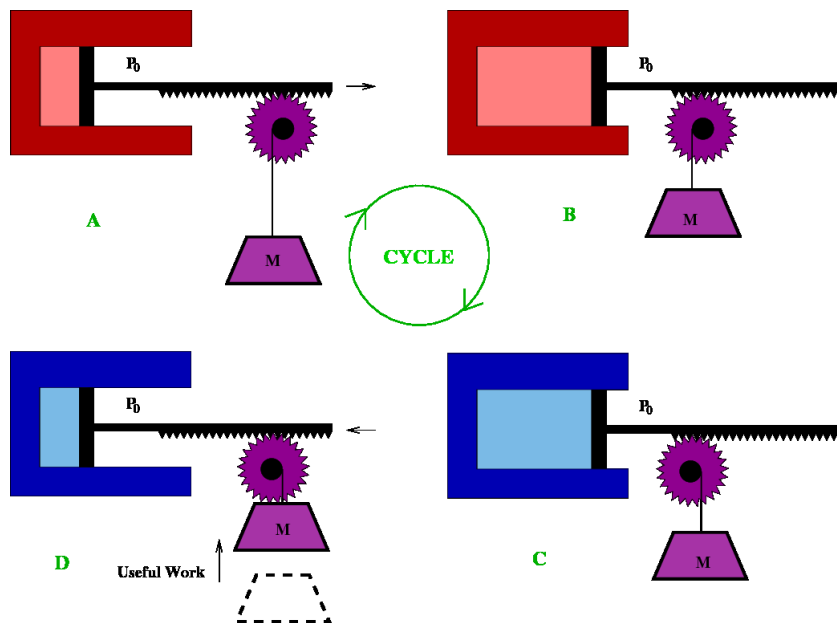
Questions about heat engines and pumps are often concerned with the most efficient possible engines, not with specific cycles. Examples of such questions can be found in the section on [Carnot engines](#).

References

- (Mandl 5.2)
- Adkins 4.2, 4.8
- Zemansky 6.1-5



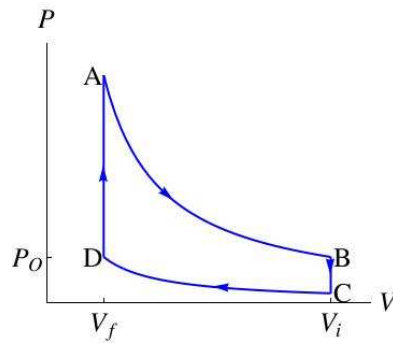
2.1.1 More extensive introduction to Heat Engines



It is easy to turn heat into work. The first stage (A→B) of the picture above illustrates the process: hot gas compressed above atmospheric pressure will expand and the movement of the piston can be harnessed to do work. If the expansion is isothermal the gas will draw heat from the reservoir and convert it into work.

But it is not so easy to continue. To re-compress the gas we would need to do an equivalent amount of work! A useful heat engine is not a one-off stroke, it is a cyclical process during which the system periodically returns to its initial state, and the process can be repeated again and again.

To continue the cycle, we can cool the gas (B→C), after which it can be compressed with less work than before (C→D). If we cool it enough, we can even get the atmosphere to do work on it during the compression phase, as suggested above. Or we might need to supply some work externally, but less than we got out during the main power stroke (A→B). Finally we heat the gas again and repeat the cycle. On returning to A, the engine is unchanged but the surroundings are not. The mass has been raised (useful work has been obtained), heat has been supplied from the hot reservoir (D→B), and, crucially, *waste heat has been supplied to the cold reservoir* (B→D). By conservation of energy, of course, the net work done on the gas equals the difference in the heat supplied and the heat discarded.



This is a crude approximation of a Stirling engine, in which the gas cycles between two reservoirs. $A \rightarrow B$ and $C \rightarrow D$ are shown as isothermal expansion and contraction, and the other two processes as isochoric (constant volume). The net work done by the gas is the area within the curve; the parameters chosen for the sketch are somewhat unrealistic. The gas in the cylinder is called the *working fluid*. By drawing the cycle with solid lines on a PV diagram, we are implicitly assuming quasi-static, frictionless processes—rather a strong idealisation!

Most other engines do not actually keep the same working fluid throughout, for instance drawing in steam from a reservoir and getting rid of exhausts, but the concept of a cycle with the initial state recurring periodically is common to all.

The Newcomen engine used steam as the working fluid, and cold water to condense it making for a powerful return stroke with essentially a vacuum in the cylinder. Internal combustion engines use the Otto or Diesel cycles; in these ignition of the fuel-air mix takes place when the gas is compressed and takes the place of contact with a hot reservoir. These have an extra (constant pressure) stroke in which the piston drives out the exhaust gases and draws in air and fuel. In the absence of heat reservoirs, the main working strokes of the Otto and Diesel cycles are adiabatic rather than isothermal.

It is also important that real engines run continuously, and most make use of the momentum of a flywheel (or of the driven vehicle) to power the compression phase.

[This link](#), courtesy of Xing Min Wang, has clear and helpful animations of the idealised Otto, Diesel and Carnot cycles.

[Animated Engines](#) has animations of a large variety of realistic engines, though without the accompanying cycles.

2.1.2 Example: The Otto cycle

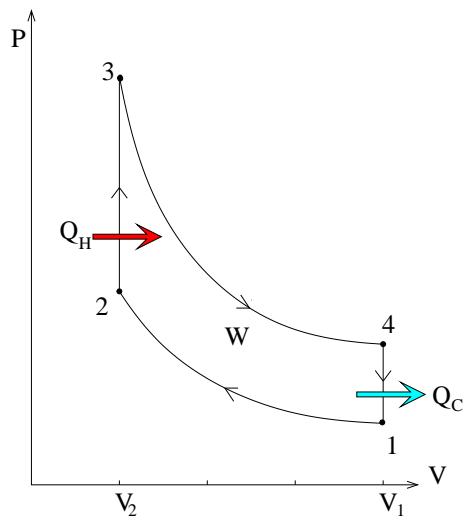
Here is a particular example of a heat engine - the Otto cycle, which approximates the working cycle of a car engine. The work done is the area enclosed by the curve in the $P - V$ plane. The expansion and compression strokes are adiabatic, so heat enters and leaves only during the constant volume phases. (This ignores the exhaust stroke, which can be modelled as a horizontal line from point 1 left and then right again.)

[This link](#), courtesy of Xing Min Wang, has clear and helpful animations of the idealised Otto, Diesel and Carnot cycles.

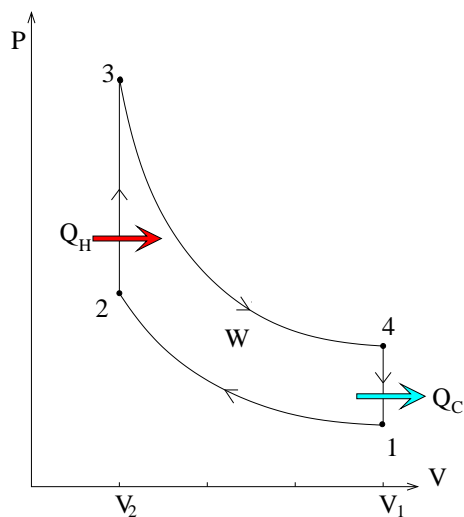
[Animated Engines](#) has animations of a large variety of realistic engines, though without the accompanying cycles.

The efficiency of a reversible Otto cycle for an ideal gas is

$$\eta = 1 - \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$



Try to prove it yourself. More details are given [here](#).



Answer For the adiabatic strokes, $Q = 0$ and $W = c_V(T_f - T_i)$. (See a [previous example](#).)

For the isochoric (constant volume) paths, $W = 0$ and $Q = c_V(T_f - T_i)$.

Also

$$T_2 = \left(\frac{V_1}{V_2}\right)^{\gamma-1} T_1 \quad \text{and} \quad T_3 = \left(\frac{V_1}{V_2}\right)^{\gamma-1} T_4$$

The total work done **by** the system is

$$W = -(W_{12} + W_{34}) = c_V(T_1 - T_2 + T_3 - T_4)$$

so

$$\eta = \frac{W}{Q_H} = \frac{T_1 - T_2 + T_3 - T_4}{T_3 - T_2} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

2.2 The Second Law of Thermodynamics

Take-home message: You can't pass heat from the cooler to the hotter

Try it if you like but you far better notter

'Cos the cold in the cooler will get hotter as a ruler

'Cos the hotter body's heat will pass to the cooler

Courtesy of Flanders and Swann (full text reproduced, legally I hope, [here](#)..)

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 a 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. See [here](#) for details.

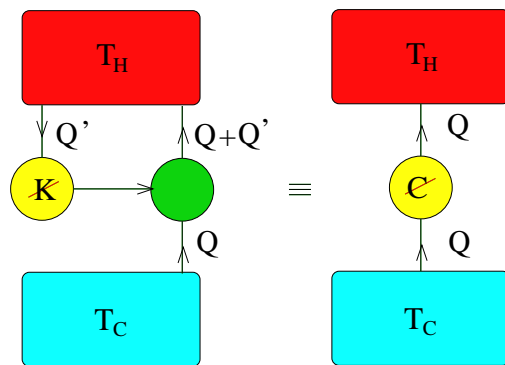
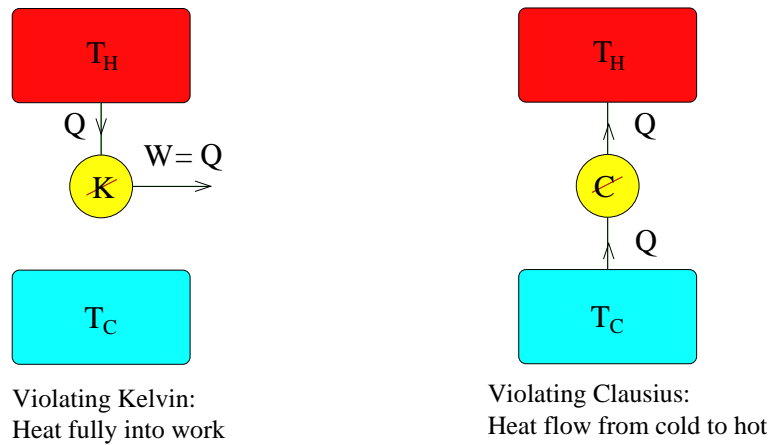
References

- (Mandl 2.1)
- Bowley and Sánchez 2.2
- Adkins 4.3
- Zemansky 6.6-8

2.2.1 Equivalence of Kelvin and Clausius statements of 2nd law.

The two [statements](#) of the second law may not appear to have anything to do with one another, but in fact each one implies the other.

The top line shows yellow engines representing hypothetical engines violating each of the two statements of the second law. The second line shows that an engine which violates Kelvin's statement, together with a normal heat pump, violates Clausius's statement. A similar drawing can be used to show that a pump which violates Clausius's statement, together with a normal heat engine, violates Kelvin's statement. Hence the two statements—which seem quite different—are actually equivalent.



2.3 Carnot cycles

Take-home message: The efficiency of a Carnot engine is independent of its construction, and no irreversible engine can beat it.

A Carnot engine is, simply, a **reversible** engine acting between only two heat reservoirs. That means that all processes are either isothermal (heat transfer at a constant temperature) or adiabatic (no heat transfer). By contrast the Otto cycle, which has heating at constant volume, would need a whole series of heat reservoirs at incrementally higher temperatures to carry out the heating reversibly.

Carnot's theorem says that a reversible engine is the most efficient engine which can operate between two reservoirs. If you want to see the proof, see [here](#). An equally important corollary is that **any** reversible engine working between two heat reservoirs has the **same** efficiency as any other, irrespective of the details of the engine.

Much is made of the fact that the Carnot engine is the most efficient engine. Actually, this is not mysterious. First, if we specify only two reservoirs, then all it says is that a reversible engine is more efficient than an irreversible engine, which isn't surprising (no friction...) Second, we will see that the efficiency of a Carnot engine increases with the temperature difference between the reservoirs. So it makes sense to use only the hottest and coldest heat baths you have available, rather than a whole series of them at intermediate temperatures. But the independence of the details of the engine is rather deeper, and has far-reaching consequences.

As a result, if we can calculate the efficiency for one Carnot engine, we know it for all. We can calculate it for an ideal gas Carnot cycle, and find

$$\eta_{\text{carnot}} = 1 - \frac{T_C}{T_H},$$

details [here](#). Hence this is true for *all* Carnot engines.

By comparing with the definition of the [efficiency of any heat engine](#), $\eta = W/Q_H = 1 - Q_C/Q_H$, we get the even more useful relation:

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H}.$$

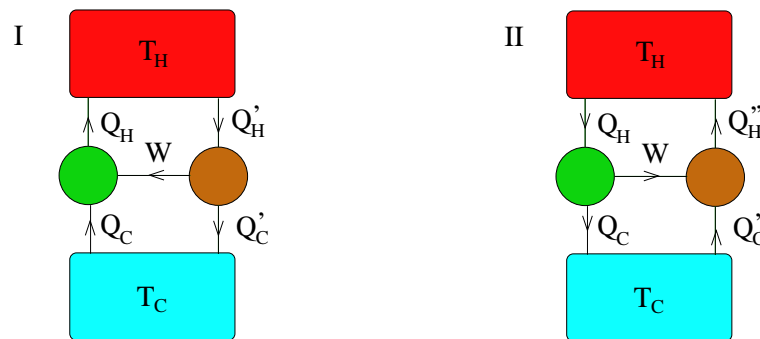
See here for [examples](#) of questions about Carnot heat engines.

Carnot developed the concept of [reversibility](#) and showed that no engine could be more efficient than a reversible one before either the first or second law of thermodynamics had been formulated! See [here](#) for a link to his essay, and to a good description of his contribution to thermodynamics.

References

- Mandl 5.2
- Bowley and Sánchez 2.3
- Adkins 4.2, 4.5
- Zemansky 7.1-4

2.3.1 Carnot wins



In the above the green engines/pumps are Carnot, and the brown ones are irreversible. Because the Carnot engine is reversible, if the engine efficiency is η_C , the pump efficiency is $1/\eta_C$. (See [here](#) for details.)

I) In the first case, a Carnot pump is driven by an engine. Overall, to avoid violating Clausius's statement of the second law, there must be no net heat transfer to the hot reservoir, so $Q'_H \geq Q_H$. Also, by conservation of energy, $Q_H - Q_C = Q'_H - Q'_C = W$. Thus

$$\frac{W}{Q'_H} = \frac{Q_H}{Q'_H} \frac{W}{Q_H}$$

so $\eta_{\text{engine}} \leq \eta_{\text{carnot}}$

II) In the second case, a Carnot engine drives a pump. Now we need $Q_H \geq Q_H''$. Thus

$$\frac{Q_H''}{W} = \frac{Q_H''}{Q_H} \frac{Q_H}{W}$$

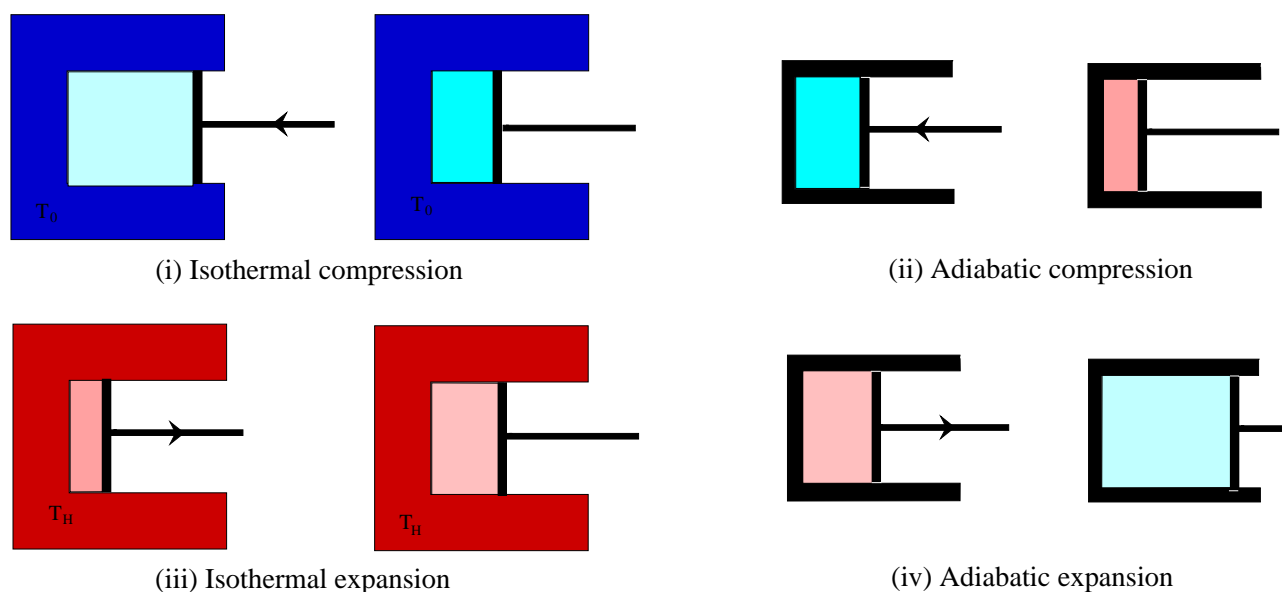
so $\eta_{\text{pump}} \leq \frac{1}{\eta_{\text{carnot}}}$

So no engine can be more efficient than a Carnot engine, and no pump can be more efficient than a Carnot pump.

If the brown pumps were in fact reversible, there could be no overall heat flow, since heat flow from a hot to a cold body is an irreversible process. In that case the inequalities would become equalities.

Thus **any** reversible engine working between two heat reservoirs has the **same** efficiency as any other.

2.3.2 Efficiency of ideal gas Carnot cycle



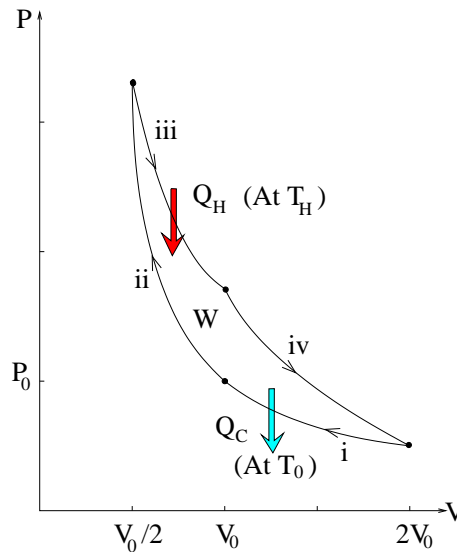
Above we see the four steps which make up an ideal gas Carnot cycle, two isothermal, (i) and (iii), and two adiabatic, (ii) and (iv). Below the cycle is sketched on a $P - V$ plot.

We have already analyzed this particular cycle (see [here](#).) We worked out the work for the four steps. We note further that the heat exchanged during the isothermal steps is just minus the work done, since the internal energy is unchanged.

Thus we have $W = nR \ln 2(T_H - T_0)$ and (from stage iii) $Q_H = nRT_H \ln 2$, so

$$\eta = \frac{W}{Q_H} = 1 - \frac{T_0}{T_H}.$$

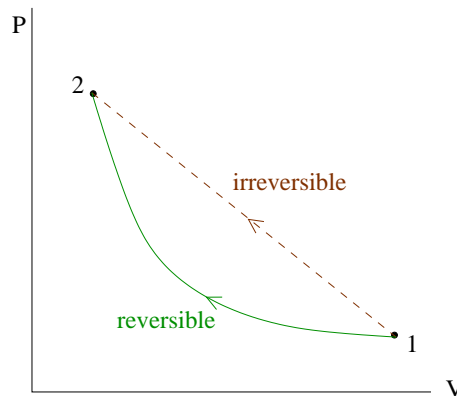
Note this cycle wasn't general, because we chose to make both the isothermal and adiabatic stages volume-halving. But form of the answer **is** general.



2.3.3 Reversible processes

Imagine a cylinder, with a perfectly smooth piston, which contains gas. If you push with a force only just large enough to overcome the internal pressure, the volume will start to decrease slowly. Then if you decrease the force only slightly, the volume will start to increase. This is the hallmark of a reversible process: an infinitesimal change in the external conditions reverses the direction of the change. Heat flow is only reversible if the temperature difference between the bodies is infinitesimally small.

Reversible processes require the absence of friction or other hysteresis effects. They must also be carried out infinitesimally slowly. Otherwise pressure waves and finite temperature gradients will be set up in the system, and irreversible dissipation and heat flow will occur.



Because reversible processes are very slow, the system is always very nearly in equilibrium at all times. In that case all its state variables are well defined and uniform, and the state of the system can be represented on a plot of, for instance, pressure versus volume. A finite reversible process passes through an infinite set of such states, and so can be drawn as a solid line on the plot. During an irreversible process the system is not in an equilibrium state, and so cannot be represented on the plot; an irreversible process is often drawn as a straight dotted line joining the initial and final equilibrium states. The work done during the process is *not* then equal to the area under the line, but will be greater than that for the corresponding reversible process.

2.3.4 Heat engine examples

The master-equations for generic heat-engine problems are the conservation of energy and the heat-temperature relation for a Carnot engine:

$$W = Q_H - Q_C \quad \text{and} \quad \frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

The question will give you one of Q_H , Q_C and W , and the master-equations give you the other two.

Try these problems for yourself before checking the detailed answers!

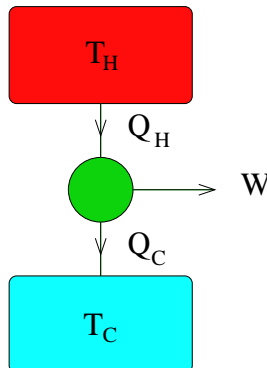
- *Ex. 1* A power station contains a heat engine operating between two heat reservoirs, one consisting of steam at 100°C and the other consisting of water at 20°C. What is the maximum amount of electrical energy which can be produced for every Joule of heat extracted from the steam?

Answer: 0.21 J. Details [here](#).

- *Ex. 2* When a fridge stands in a room at 20°C, the motor has to extract 500 W of heat from the cabinet, at 4°C, to compensate for less than perfect insulation. How much power must be supplied to the motor if its efficiency is 80% of the maximum achievable?

Answer: 2.9 J. Details [here](#).

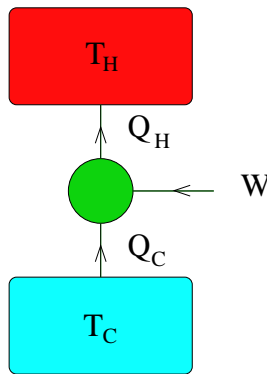
Ex. 1 A power station contains a heat engine operating between two heatone consisting of steam at 100°C and the other consisting of water at 20°C. What is the maximum amount of electrical energy which can be produced for every Joule of heat extracted from the steam?



The maximum efficiency comes from using a Carnot (reversible) engine, for which $Q_H/Q_C = T_H/T_C$, and so

$$W = Q_H - Q_C = Q_H \left(1 - \frac{T_C}{T_H} \right)$$

With $T_H = 373 \text{ K}$ and $T_C = 293 \text{ K}$, for every Joule of heat extracted from the hot reservoir ($Q_H = 1 \text{ J}$), $W_{\text{max}} = 0.21 \text{ J}$.



Ex. 2 When a fridge stands in a room at 20°C , the motor has to extract 500 W of heat from the cabinet, at 4°C , to compensate for less than perfect insulation. How much power must be supplied to the motor if its efficiency is 80% of the maximum achievable?

The maximum efficiency comes from using a Carnot (reversible) fridge, for which $Q_H/Q_C = T_H/T_C$. Here Q_C is known, and so

$$W = Q_H - Q_C = Q_C \left(\frac{T_H}{T_C} - 1 \right)$$

(In this question W , Q_H and Q_C will refer to energy transfer per second, measured in Watts.) With $T_H = 293\text{ K}$ and $T_C = 277\text{ K}$, $Q_C = 500\text{ W}$ gives $W_{\text{max}} = 29\text{ W}$. However the real fridge works at 80% of the maximum efficiency, so $W = (29/0.8) = 36\text{ W}$

2.4 Thermodynamic Temperature

Take-home message: The fact that the efficiency of a Carnot engine depends only on the operating temperatures provides an alternative way of defining a temperature scale.

If we hadn't already developed a good temperature scale, we could use the fact that the efficiency of a Carnot engine depends only on the operating temperatures to develop one.

Given a heat bath at a reference temperature (eg a very large triple-point cell) we could use the efficiency of a Carnot engine working between it and another body to label that other body's temperature.

By considering compound Carnot engines it can be shown that the dependence of the efficiency on temperature θ , **no matter what scale is used for the latter**, has the form

$$\eta_{\text{carnot}} = 1 - \frac{\Theta(\theta_C)}{\Theta(\theta_H)}$$

where $\Theta(\theta)$ is some function of θ . Thus Θ itself is a perfectly good temperature scale, which vanishes at absolute zero: this is called the **thermodynamic temperature**. (See [here](#) for details.)

The reason you haven't heard of it is that, if we compare it with the efficiency expressed in terms of the ideal gas temperature scale,

$$\eta_{\text{carnot}} = 1 - \frac{T_C}{T_H}$$

we see that Θ is simply proportional to the ideal gas temperature, and will therefore be identical if we set $\Theta_{\text{triple}} = 273.15$. Since a nearly ideal gas is more achievable than a reversible heat engine, that's the name that has finally stuck.

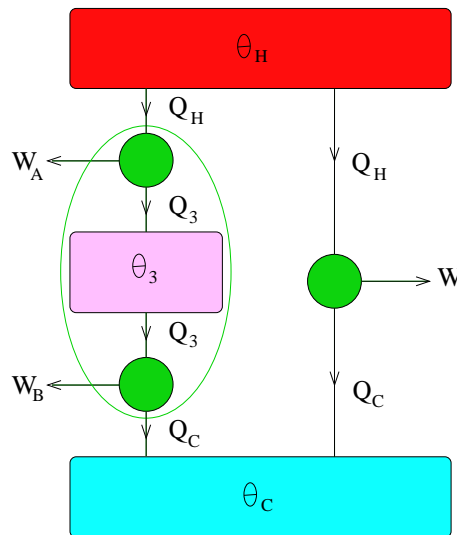
References

- Bowley and Sánchez 2.3-4
- Adkins 4.6
- Zemansky 7.5

2.4.1 Construction of thermodynamic temperature

Below we have two engines (one consisting of two more in series) working between heat reservoirs at θ_H and θ_C . Remember θ_H etc refer to temperatures on some unspecified scale. We know that the efficiency of a Carnot engine working between θ_H and θ_C depends only on θ_H and θ_C , but we don't know how: let us define a function $f(\theta_H, \theta_C)$ such that

$$Q_C = f(\theta_C, \theta_H) Q_H \quad \text{so} \quad \eta = 1 - f(\theta_C, \theta_H).$$



Now considering the two engines in series,

$$Q_3 = f(\theta_3, \theta_H) Q_H \quad \text{and} \quad W_A = (1 - f(\theta_3, \theta_H)) Q_H$$

$$\text{also } Q_C = f(\theta_C, \theta_3) Q_3 = f(\theta_C, \theta_3) f(\theta_3, \theta_H) Q_H \quad \text{and} \quad W_B = (1 - f(\theta_C, \theta_3)) f(\theta_3, \theta_H) Q_H$$

$$\text{so } W_A + W_B = (1 - f(\theta_C, \theta_3) f(\theta_3, \theta_H)) Q_H$$

But everything within the green oval in the diagram can be considered as a single, composite, Carnot engine, so its output must be the same as the simple one for the same heat flow Q_H : $W_A + W_B = W$. Thus we can match the efficiencies of the simple and composite engines to get

$$f(\theta_C, \theta_3) f(\theta_3, \theta_H) = f(\theta_C, \theta_H).$$

This has to be true independently of the value of θ_3 , which can only be true if f factorises:

$$f(\theta_C, \theta_H) = \frac{\Theta(\theta_C)}{\Theta(\theta_H)}$$

where Θ is some function of θ

Thus we have the desired result,

$$\eta_{\text{carnot}} = 1 - \frac{\Theta(\theta_C)}{\Theta(\theta_H)}.$$

References

- Bowley and Sánchez 2.3
- Adkins 4.5-6
- Zemansky 7.5

2.5 Entropy

Take-home message: The second law leads us to define a new function of state, **entropy**. The entropy of an isolated system can never decrease.

Clausius's theorem says that if a system is taken through a cycle, 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:

$$\oint \frac{dQ}{T} \leq 0$$

This follows from [Clausius's statement](#) of the second law. The details of the proof are [here](#). The inequality becomes an equality for reversible systems:

$$\oint \frac{dQ^{\text{rev}}}{T} = 0.$$

We can verify that this holds for a system which is taken through a Carnot cycle, since there heat only enters or leave at one of two temperatures:

$$\oint \frac{dQ^{\text{rev}}}{T} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0.$$

(A less rigorous proof of Clausius's theorem, used in Bowley and Sánchez and in Zemansky, involves approximating any reversible cycle by a large number of Carnot cycles.)

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 :

$$dS = \frac{dQ^{\text{rev}}}{T}$$

and $\oint dS = 0$.

So much for cycles. What about other processes? By considering a cycle consisting of one reversible and one irreversible process, we can show that in general,

$$dQ \leq T dS.$$

(Details [here](#).) This gives rise to the most important result of all. For an **isolated system**, $dQ = 0$. So for such a system,

$$dS \geq 0.$$

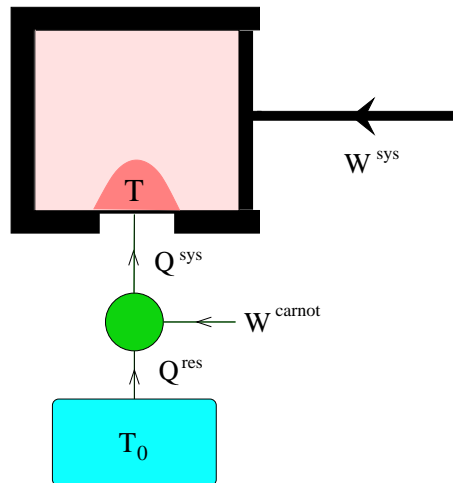
This leads to an alternative statement of the second law: **The entropy of an isolated system can never decrease.**

A system and its surroundings together (“the universe”) form an isolated system, whose entropy never decreases: any decrease in the entropy of a system must be compensated by the entropy increase of its surroundings.

References

- Bowley and Sánchez 2.5
- Adkins 5.1-3
- Zemansky 8.1-2, 8.9

2.5.1 Proof of Clausius’s theorem



In the diagram, the system is the gas in the piston. We use a Carnot heat engine/pump to add heat Q^{sys} to the system at a local, varying temperature T . During the process work W^{sys} is done on the system. (Both Q^{sys} and W^{sys} could be positive or negative.) The cold reservoir of the Carnot engine is at T_0 .

The [Kelvin-Planck statement](#) of the second law says that at the end of a complete cycle of the system, we cannot have extracted net work from the system (or else we would have turned heat into work). Looking at the figure to see how the signs of the various works are defined, that means $W^{\text{carnot}} + W^{\text{sys}} > 0$. By conservation of energy, and because the system and engine have returned to their initial states, and net work put in must end up as heat added to the reservoir: $Q^{\text{res}} \leq 0$ (less than zero because Q^{res} is defined as heat extracted).

Looking now at the Carnot engine, we see that if at some point in the cycle we add heat dQ^{sys} at temperature T , heat dQ^{res} is extracted from the reservoir, and

$$dQ^{\text{res}} = \frac{T_0}{T} dQ^{\text{sys}}.$$

Since the total heat extracted is less than zero, we have

$$Q^{\text{res}} = \oint \mathrm{d}Q^{\text{res}} = \oint \frac{T_0}{T} \mathrm{d}Q^{\text{sys}} = T_0 \oint \frac{\mathrm{d}Q^{\text{sys}}}{T} \leq 0$$

which proves the inequality: (dropping the superscript “sys”)

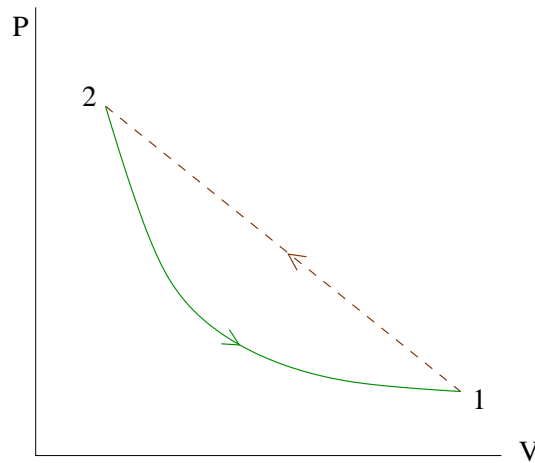
$$\oint \frac{\mathrm{d}Q}{T} \leq 0.$$

Clearly if the system is taken through a **reversible** cycle, it can be run in reverse and all quantities will simply change signs. But if Q^{res} was less than zero originally, it will be greater for the reversed cycle, implying a net extraction of work and violating the Kelvin-Planck statement. Thus for a reversible system, Q^{res} must be exactly zero, and

$$\oint \frac{\mathrm{d}Q^{\text{rev}}}{T} = 0.$$

2.5.2 Increase of entropy

Here we imagine a cycle in which we go from point 1 to point 2 by an irreversible process and back by a reversible process. (See [here](#) for an explanation of the picture.)



The entropy change for a reversible process is given by

$$S_2 - S_1 = \int_1^2 \frac{\mathrm{d}Q^{\text{rev}}}{T}$$

What can we say about an irreversible process between the same endpoints? Clearly the entropy change is the same (that’s what we mean by saying entropy is a function of state.) But if we consider a cycle involving an irreversible process from 1 to 2 and a reversible process to return to 1, we have a cycle for which Clausius’s theorem holds:

$$\begin{aligned} \oint \frac{\mathrm{d}Q}{T} &< 0 \\ \Rightarrow \int_1^2 \frac{\mathrm{d}Q^{\text{irrev}}}{T} + \int_2^1 \frac{\mathrm{d}Q^{\text{rev}}}{T} &< 0 \\ \Rightarrow \int_1^2 \frac{\mathrm{d}Q^{\text{irrev}}}{T} &< S_2 - S_1. \end{aligned}$$

Hence in general,

$$\mathrm{d}Q \leq T\mathrm{d}S,$$

and so for an **isolated system**, where $\mathrm{d}Q = 0$,

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

2.6 Examples of entropy changes

Take-home message: Spontaneous changes are always associated with entropy increase.

Below we have various examples of entropy change during various processes. From them we can draw some general conclusions. First we see in general the entropy of anything increases when it is heated, and the entropy of a gas increases when it expands at constant temperature. A common theme (to be explored in more detail later) is that an increase in entropy is associated with an increase in disorder.

Examples of spontaneous processes are the flow of heat from a hotter to a colder body (see Ex. 1) and the free expansion of a gas (see Ex. 4). In both of these, the total entropy increases (though that of parts of the system may decrease). This is completely general: spontaneous processes are those which increase entropy.

Since heat flow from hotter to colder bodies is irreversible, reversible processes must involve heat flow between bodies of the *same* temperature. It follows that any entropy change of the system $\mathrm{d}S_{\text{sys}} = \mathrm{d}Q^{\text{rev}}/T$ must be exactly balanced by that of the heat bath which provided the heat: $\mathrm{d}S_{\text{res}} = -\mathrm{d}Q^{\text{rev}}/T$. Thus the entropy change of the universe during reversible processes is zero.

During an adiabatic process no heat flows. Thus from $\mathrm{d}S = \mathrm{d}Q^{\text{rev}}/T$ we see that the entropy change of a system during for a **reversible, adiabatic** process is zero. But note that **both** qualifiers are needed; the entropy of a non-isolated system can change during a reversible process (and the entropy change of the surroundings will compensate), and an irreversible change to an isolated system will increase the entropy (see Ex. 1&4).

- The entropy of the universe always increases during spontaneous changes.
- During reversible changes the entropy of the system may change, but that of the universe stays constant.
- It follows that spontaneous changes are always irreversible
- During reversible, adiabatic changes the entropy of the system is constant.

For an ideal gas, we can show that when the temperature and pressure change from (T_1, V_1) to (T_2, V_2) , the entropy change is given by

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) + nc_v \ln \left(\frac{T_2}{T_1} \right).$$

Try these problems for yourself before checking the detailed answers!

- *Ex. 1* Two identical blocks of iron, one at 100°C and the other at 0°C, are brought into thermal contact. What happens? What is the total entropy change? (Assume the heat capacity of each block, C , is constant over this temperature range, and neglect volume changes)

Answer: Both blocks end up at 50°C and the entropy change is $0.024C$. More details [here](#).

- *Ex. 2* Two identical blocks of iron, one at 100°C and the other at 0°C, are brought into thermal contact. What is the maximum work that can be extracted from the hot block in the absence of other heat sinks?

Answer: The final temperature is 46°C and 14% of the energy lost by the hot block is available to do work. More details [here](#).

- *Ex. 3 Heat engines revisited* From the law of non-decrease of entropy, show that the maximum efficiency of a heat engine operating between two reservoirs at T_H and T_C occurs when the engine is reversible.

Answer [here](#).

- *Ex. 4* n moles of an ideal gas at temperature T_0 are originally confined to half of an insulated container by a partition. The partition is removed without doing any work. What is the change in entropy?

Answer: $\Delta S = nR \ln 2$. More details [here](#).

- *Ex. 5* An insulated container is originally divided in half by a partition, and each half is originally occupied by n moles of an different ideal gas at temperature T_0 . The partition is removed without doing any work. What is the change in entropy?

Answer: $\Delta S = 2nR \ln 2$. More details [here](#).

References

- (Mandl 2.1)
- Bowley and Sánchez 2.7
- Adkins 5.5-6
- Zemansky 8.11-13

2.6.1 Ex. 1

Two identical blocks of iron, one at 100°C and the other at 0°C, are brought into thermal contact. What happens? What is the total entropy change? (Assume the heat capacity of each block, c , is constant over this temperature range, and neglect volume changes)

We know what happens: heat flows from the hot to the cold body till they reach the same temperature; conservation of energy requires that this will be at 50°C. Why does heat transfer occur? If heat dQ is transferred from a hot body at T_H to a cold one at T_C , the entropy decrease of the hot body is $dS_H > -dQ/T_H$, and the entropy increase of the cold body is $dS_C > dQ/T_C$. So the total entropy change is

$$dS = dS_H + dS_C > \left(\frac{1}{T_C} - \frac{1}{T_H} \right) dQ > 0$$

So the decrease in entropy of the hot block is more than compensated by the increase in entropy of the cold block. The spontaneous flow of heat is associated with an overall entropy increase, and the two blocks exchange heat till their combined entropy is maximised.

What is the overall entropy change for the total process? Here we have to use a trick. We can't calculate entropy changes for irreversible processes directly; we need to imagine a reversible process between the same endpoints. For the heating or cooling of a block, this would involve bringing it in contact with a series of heat baths at infinitesimally increasing or decreasing temperatures, so that the temperature difference between the heat bath and the block is always negligible and the entropy change is zero.

During this process, the heat transfer and the infinitesimal temperature change are related by $dQ^{\text{rev}} = C dT$ and so

$$\Delta S = \int_1^2 \frac{dQ^{\text{rev}}}{T} = C \int_{T_1}^{T_2} \frac{dT}{T} = C \ln \left(\frac{T_2}{T_1} \right)$$

Thus the total entropy change is

$$\begin{aligned} \Delta S &= \Delta S_C + \Delta S_H = C \ln \left(\frac{T_f}{T_C} \right) + C \ln \left(\frac{T_f}{T_H} \right) = C \ln \left(\frac{T_f^2}{T_H T_C} \right) \\ &= C \ln \left(\frac{323^2}{273 \times 373} \right) = 0.024C \end{aligned}$$

Note this is positive, and also that entropy has the same units as heat capacity, Joules/Kelvin.

2.6.2 Ex. 2

Two identical blocks of iron, one at 100°C and the other at 0°C, are brought into thermal contact. what is the maximum work that can be extracted from the hot block in the absence of other heat sinks?

Remember, we can't just extract heat from the hot block and turn it into work; the entropy of the block would decrease without any compensating increase elsewhere. We need to add at least enough heat to the cold block so that its entropy increases by as much as that of the hot block decreases. (Work can always be used to do things which don't increase the entropy of the universe, such as lifting a weight.) Once the two blocks are at the same temperature, no further work can be extracted.

At that point the entropy change of the two blocks together, from the [previous example](#), is

$$\Delta S = c \ln \left(\frac{T_f^2}{T_H T_C} \right) \geq 0$$

The lowest final temperature is that for which $\Delta S = 0$, ie $T_f = \sqrt{T_H T_C} = 319 \text{ K} = 46^\circ\text{C}$. (Any lower and ΔS would go negative, which isn't allowed.) So although the total heat loss of the hot block is $Q_H = c(T_H - T_f)$, the work extracted is only the difference between this and the heat gained by the cold block, $Q_C = c(T_f - T_C)$, namely $W = c(T_H + T_C - 2T_f)$. In this case, the efficiency is

$$\eta = \frac{W}{Q_H} = \frac{(T_H + T_C - 2T_f)}{(T_H - T_f)} = 0.144.$$

Only 14% of the heat lost by the hot block was available to do work! Note that the maximum efficiency was obtained from a **reversible** process.

2.6.3 Ex. 3

Heat engines revisited: From the law of non-decrease of entropy, show that the maximum efficiency of a heat engine operating between two reservoirs at T_H and T_C occurs when the engine is reversible.

This is a bit circular, as we used the properties of Carnot engines to derive this form of the second law! However we will see later in the course that it can be independently derived using statistical methods.

The change in entropy of the two reservoirs, which must be non-negative, is

$$\Delta S = \Delta S_C + \Delta S_H = \frac{Q_C}{T_C} - \frac{Q_H}{T_H} \geq 0 \quad \Rightarrow \quad \frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}$$

with the equality being for $\Delta S = 0$, *ie* for a reversible process. So the efficiency is

$$\eta = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H} \leq 1 - \frac{T_C}{T_H}$$

This is maximum when the equality is satisfied, *ie* for a reversible engine.

2.6.4 Ex. 4

n moles of an ideal gas at temperature T_0 are originally confined to half of an insulated container by a partition. The partition is removed without doing any work. What is the final change in entropy?

First, we must resist the temptation to say $dQ = 0$ (because process is adiabatic) hence $dS = 0$. In fact $dS = dQ^{\text{rev}}/T$ and this is not a reversible process. To solve this problem, we need to find a reversible process linking the same two endpoints. We've already seen this; the process is a reversible isothermal expansion (see [here](#).) For such an expansion $Q = -W = nRT_0 \ln(V_2/V_1)$ so $\Delta S = Q/T_0 = nR \ln 2$ (details of the work calculation [here](#)).

This is rather subtle; make sure you understand the difference between the actual process (with $Q = 0$ and $W = 0$) and the reversible process for which we could calculate the entropy change (with $Q = -W \neq 0$). Remember, Q and W are not functions of state - only the sum is.

2.6.5 Ex. 5

An insulated container is originally divided in half by a partition, and each half is originally occupied by n moles of an different ideal gas at temperature T_0 . The partition is removed without doing any work. What is the change in entropy?

Since these are ideal gases, they do not interact. Each species is oblivious of the existence of the other and the entropy change for each is just the same as in the free expansion of [Ex. 4](#). Thus the total entropy change is given by $\Delta S = 2nR \ln 2$. Note that the total mixing - which we know will happen eventually - is exactly the change which maximises the entropy.

2.7 The Fundamental Thermodynamic Relation

Take-home message: Remember this equation!

The [first law for infinitesimal changes](#) says $dE = dQ + dW$. Since it is obviously true for reversible changes, we have $dE = dQ^{\text{rev}} + dW^{\text{rev}}$. We have already found expressions for [reversible](#)

work for a variety of systems; now we have one for reversible heat transfer too: $dQ^{\text{rev}} = TdS$. So we can put these together to form an expression for dE which only involves functions of state. For a hydrodynamic system, for instance,

$$dE = TdS - PdV.$$

This is called **the fundamental thermodynamic relation**. It involves only functions of state, so it is true for **all** changes, not just reversible ones.

For other systems, $-PdV$ is replaced by the appropriate expression for dW^{rev} , eg Γdl for a stretched string.

The significance of this equation should become clear as the course continues: it is one of the most important half-dozen equations we will meet.

References

- (Mandl 4.1)
- Bowley and Sánchez 2.5
- Adkins 5.4
- Zemansky 8.14

2.8 Thermodynamic potentials

Take-home message: Other quantities can be defined which, under common experimental conditions, are more relevant than the energy.

Let's look again at the fundamental thermodynamic relation for a hydrodynamic system: $dE = TdS - PdV$.

This suggests that the natural variable in which to express E are S and V : $E = E(S, V)$. That means that energy will be unchanged for processes at constant volume and entropy—not the most common experimental conditions. It is useful to introduce other functions of state, called “thermodynamic potentials”, which are conserved, or whose change is easily calculated, in common experimental conditions.

These are

- **Enthalpy:**

$$H = E + PV \quad \text{so} \quad dH = dE + dPV + PdV \\ = TdS + VdP$$

At constant pressure (such as chemical reactions in a test tube), $dP = 0$ and so $dH = dQ^{\text{rev}}$. Heats of reaction are usually measured as enthalpies of reaction.

- **Helmholtz free Energy:**

$$F = E - TS \quad \text{so} \quad dF = dE - dTS - TdS \\ = -SdT - PdV$$

The Helmholtz free energy is constant at constant temperature and volume. It plays a key role in statistical physics.

- **Gibbs Free Energy:**

$$G = E - TS + PV \quad \text{so} \quad dG = -SdT + VdP$$

The Gibbs free energy is constant if the temperature and pressure are constant. These are the conditions under which phase transitions (melting, boiling) take place, and are also relevant to chemical equilibrium.

Note that Enthalpy and Gibbs free energy are only relevant to hydrodynamic systems for which $dW^{\text{rev}} = -PdV$. However the energy and the Helmholtz free energy is more general, with $dE = TdS + dW^{\text{rev}}$ and $dF = -SdT + dW^{\text{rev}}$

References

- Mandl 4.4-5
- Bowley and Sánchez 2.6
- Adkins 7.1
- Zemansky 10.1-3 (Warning: Zemansky uses A for the Helmholtz free energy!)

2.9 The approach to equilibrium

Take-home message: Spontaneous changes maximise the entropy of an isolated system, but minimise the appropriate free energy of non-isolated systems.

We have seen that, for an isolated system, the entropy change will always be greater than or equal to zero. But more than that, we have seen in specific examples that if a change can take place which increases the entropy, it will. A hot and a cold block brought in to contact *will* exchange heat till they are at the same temperature, and not stop half way. Two gases which are allowed to mix *will* mix fully, and not just partially. In both cases the final state maximises the entropy with respect to the free parameter - the amount of heat exchanged, or the degree of mixing.

But what about non-isolated systems? Obviously the entropy of the [universe](#) increases. But it would be convenient if we could describe what happens by referring only to the system, and not the surroundings. In fact there is a way. If the external temperature is T_0 and pressure P_0 , we can define the quantity

$$A = E - T_0S + P_0V,$$

called the **availability**, and we find that it always decreases during a spontaneous change. (See [here](#) for details.)

For a process with starts and ends at the temperature and pressure of the surroundings, the initial and final availabilities are just the initial and final **Gibbs free energy**, so any such process minimises G .

For a process which starts and ends at the temperature of the surroundings and which is at constant volume, $\Delta V = 0$ and so $\Delta A = \Delta F$. Such a process minimises the Helmholtz free energy F .

For an isolated system, both V and E must be constant, so a decrease of A simply means an increase of S , as it should!

In all of the above, we are implicitly assuming that the system has unspecified internal degrees of freedom which are initially out of equilibrium, such as un-mixed gases or unreacted chemicals, or regions of different temperatures or pressures (for thermally- or mechanically-isolated systems, respectively). Otherwise the state of the system is fully specified and no evolution can happen.

Isolated (Constant energy)	isothermal Constant volume	isothermal Constant pressure
S Maximised	F Minimised	G Minimised

References

- Mandl 4.2
- Bowley and Sánchez 2.9
- Adkins 10.2
- Zemansky 10.3 (Warning: Zemansky uses A for the Helmholtz free energy!)

2.9.1 Derivation of availability

Consider a system in thermal contact with its surrounding at T_0 , and at the pressure of the surroundings P_0 . What spontaneous changes will occur? Taking the surroundings and the system together, the entropy will be maximised. What does that mean for the system?

Imagine a spontaneous change during which Q is absorbed by the system, and the volume change ΔV , so that work $W = -P_0\Delta V$ is done on the system. Then from the first law, $Q = \Delta E + P_0\Delta V$. The total change in entropy has two parts, ΔS for the system and $-Q/T_0$ for the surroundings. So

$$\begin{aligned}\Delta S_{\text{tot}} &= \Delta S - \frac{Q}{T_0} = \frac{T_0\Delta S - \Delta E - P_0\Delta V}{T_0} \geq 0 \\ &\Rightarrow \Delta(E - T_0S + P_0V) \leq 0\end{aligned}$$

The quantity $A = E - T_0S + P_0V$ is called the **availability**, and it always decreases during a spontaneous change.

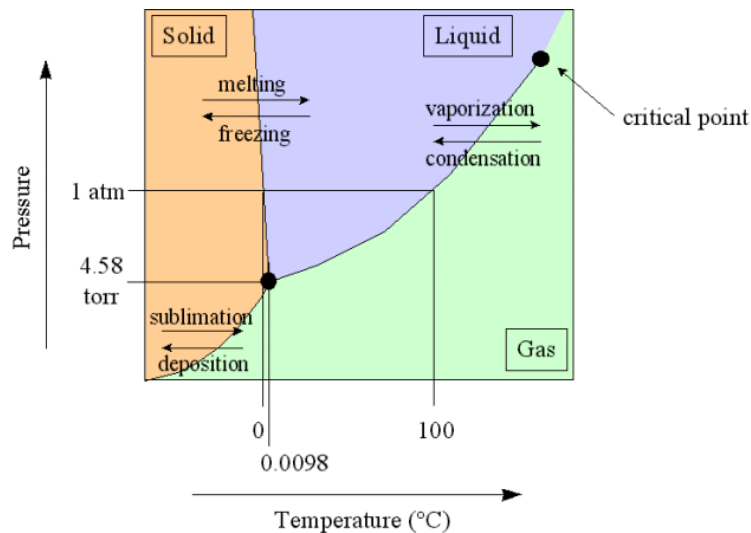
2.10 Use of Gibbs Free Energy: Phase Transitions

Take-home message: The Gibbs free energies of two coexisting phases is the same.

We are interested in the cases where two phases of the same substance can coexist. An example is ice in water at 0°C: if no heat is exchanged with the surroundings, the mixture will persist indefinitely.

In practical cases we are interested in charting the behaviour of the substance as a function of external temperature and pressure. For most choices, only one phase will persist at equilibrium - water, or ice, or vapour, for example. But for certain choices, two or even three phases may coexist.

The phase diagram for water is shown below. (Image ©M. Blaber, Florida State University)



It differs from a generic substance in the backward slope of the ice-water coexistence line: putting ice under pressure may cause it to melt, whereas most liquids close to their freezing point will freeze under pressure.

What determines the lines of phase coexistence?

Consider a system of two phases, 1 (say gas) and 2 (say liquid) at a fixed pressure and temperature.

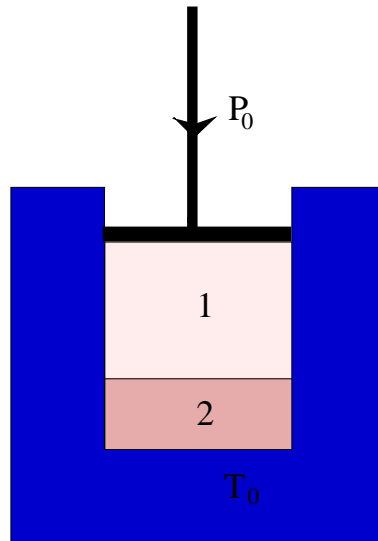
From the fact that the system will minimise its Gibbs free energy, we can [derive](#) the following condition for phase coexistence: The Gibbs free energy per unit mass in each phase is the same.

At temperatures and pressures not on the coexistence line the Gibbs free energy of one phase will be lower than the other, and only the phase with the lower energy will be present at equilibrium.

Suppose we know the location of one point on a coexistence line (for instance the melting point at atmospheric pressure). Can we discover other points - for instance, the melting point at a higher or lower pressure? The answer is yes, for very small changes: in fact we can discover the **slope** of the line:

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

where L is the latent heat of the transition for some quantity of the substance, and ΔV is the volume change of the same quantity as it undergoes the transition. This is called the **Clausius-Clapeyron equation**. (Details of the derivation [here](#).)



We can use this equation to [estimate](#) the boiling point of water at the top of Mount Everest, where the pressure is only about a third of that at sea-level, to be 82°C.

(Input data: pressure at the top of Everest is 0.36 atmospheres, the density of water vapour at 100°C is 0.598 kg/m³ and the latent heat is 2.257×10^3 J/g.)

Of course this estimate requires assuming that the phase coexistence line has negligible curvature over a fairly large range, so it is no surprise that the result is only approximate. By looking at the [phase diagram](#) above you should be able to say if the true temperature is higher or lower.

References

- Mandl 8.1-4
- Bowley and Sánchez 11.1, 11.4-5 (note they refer to the “Clapeyron Equation”)
- Adkins 10.3-5
- Zemansky 11.3-4

2.10.1 Proof of equality of Gibbs free energy at a phase coexistence line

If the system is in equilibrium at a fixed pressure and temperature, the Gibbs free energy must be a minimum. That means that G will be unchanged under a further small shift of mass from one phase to the other.

Now the total Gibbs free energy is the sum of the gibbs free energy of each phase. If we introduce the “specific Gibbs free energy”, the Gibbs free energy per unit mass, and if the mass of each phase is m_1 and m_2 , we can write

$$G = m_1 g_1 + m_2 g_2$$

At equilibrium a small transfer of mass dm from one phase to the other won’t change the total G :

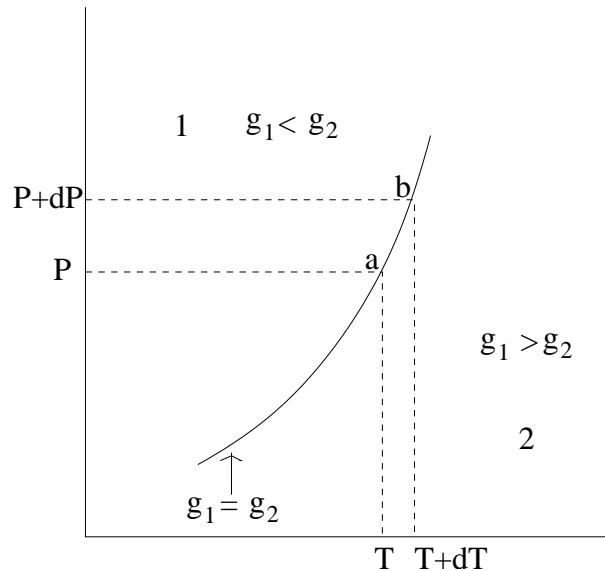
$$dG = dm_1 g_1 + dm_2 g_2 = dm g_1 - dm g_2 = 0$$

This can only be true if $g_1 = g_2$.

So the condition for phase coexistence is that the Gibbs free energy per unit mass in each phase is the same.

2.10.2 The Clausius-Clapeyron Equation

Suppose we know the location of one point on a coexistence line (for instance the melting point at atmospheric pressure). Can we discover other points - for instance, the melting point at a higher or lower pressure? The answer is yes, for very small changes: in fact we can discover the **slope** of the line.



At both a and b the two phases are in equilibrium, so the specific Gibbs free energies of the two phases at each point are the same: $g_1^{(a)} = g_2^{(a)}$ and $g_1^{(b)} = g_2^{(b)}$. So if dg is the difference in the Gibbs free energy between the two points, it is the same for both phases: $dg_1 = dg_2$. But (using small letters s and v to denote specific entropy and volume),

$$\begin{aligned} dg_1 &= -s_1 dT + v_1 dP \\ dg_2 &= -s_2 dT + v_2 dP \\ \Rightarrow (s_2 - s_1) dT &= (v_2 - v_1) dP \\ \Rightarrow \frac{dP}{dT} &= \frac{S_2 - S_1}{V_2 - V_1} \end{aligned}$$

This is called the **Clausius-Clapeyron equation**, and it relates the slope *along* the coexistence line with the change in entropy and volume of the substance as it *crosses* the line, *ie* changes phase.

This doesn't look very useful, as we can't measure entropy directly. However, using $\Delta S = Q/T$ for an isothermal process, we can find the change in entropy at a phase transition from the latent heat L , and so the more useful form of the equation is

$$\frac{dP}{dT} = \frac{L}{T\Delta V}.$$

2.10.3 Boiling point on Everest

We take the pressure at the top of Everest to be 0.36 atmospheres, the density of water vapour at 100°C to be 0.598 kg/m³ and the latent heat to be 2.257×10^3 J/g.

The change in volume of 1 gram is well approximated by just the volume of the gas phase, since the vapour is about a thousand times less dense than the liquid: $\Delta V = V_g - V_l \approx V_g = 1/\rho_g$.

So

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{L\rho_g}{T} = 3.6 \times 10^3 \text{ Pa/K}$$

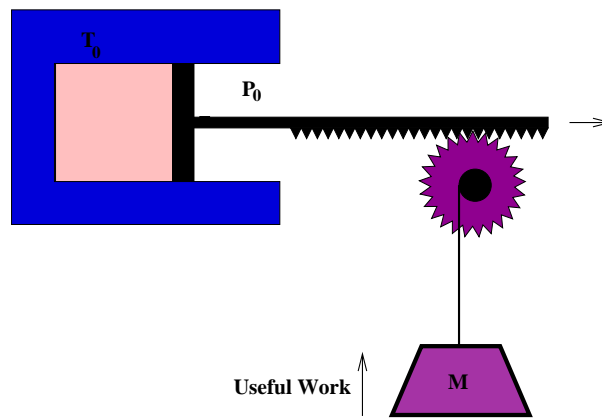
$$\Rightarrow \Delta T \approx \Delta P / (3.6 \times 10^3 \text{ Pa/K}) = -18^\circ\text{C}$$

Did you get the right numbers? If not, did you remember to convert the latent heat and the density to refer to the **same** amount of water (1 kg or 1 g).

2.11 Available work

Take-home message: The availability is a measure of the useful work which can be extracted from a system.

Here we consider the amount of useful work which can be extracted from a system which is initially out of equilibrium with its surroundings, which are at temperature T_0 and pressure P_0 .



There are two factors which limit this. One is that if the system expands, it has to overcome atmospheric pressure before doing any useful work, so $P_0\Delta V$ is wasted. The other is that if its entropy decreases (as in cooling) the entropy of the surrounding must increase enough to compensate. The system must discard heat Q to the surroundings so that $\Delta S + Q/T_0 \geq 0$.

So of the total energy decrease of the system, ΔE , the amount available to do work is

$$W^{\text{useful}} = (-\Delta E) - Q - P_0\Delta V \leq -\Delta E + T_0\Delta S - P_0\Delta V = -\Delta A$$

where the availability A is $E - T_0S + P_0V$.

The equality is satisfied for reversible processes, which maximises the useful work available. (To cool reversibly with only a single cold reservoir would require the use of a heat engine to extract the heat, rather than the direct transfer depicted above.)

This explains why the availability, which we have met in a slightly different [context](#), is so called.

Remember that it is the temperature and pressure of the surroundings that enter, not that of the system (though they end up the same).

Follow [this link](#) for an example.

References

- Mandl 4.6
- Adkins 10.2

2.11.1 Example of available work

What is the maximum amount of work theoretically available from one mole of monatomic ideal gas, cooled at constant volume from an initial temperature T to the temperature of the surroundings T_0 ?

$$W^{\max} = -\Delta A = -\Delta E + T_0 \Delta S$$

Now $\Delta E = -C_V(T - T_0)$ for an [ideal gas](#) and $\Delta S = -C_V \ln(T/T_0)$ (see [here](#).) So

$$W^{\max} = C_V \left(T - T_0 - T_0 \ln \frac{T}{T_0} \right)$$

For 1 mole, $C_V = 3R/2$.

The rest of the energy is discarded to the surroundings to ensure no overall decrease in entropy. Of course this is simple enough that we could have done the calculation directly from entropy considerations, taking the surroundings into account explicitly. Compare with [this example](#).

2.12 Maxwell's Relations

Take-home message: Remember these relations!

As we have [seen](#), the fundamental thermodynamic relation $dE = TdS - PdV$ implies that the natural variable in which to express E are S and V : $E = E(S, V)$.

That means that on purely mathematical grounds, we can write

$$dE = \left(\frac{\partial E}{\partial S} \right)_V dS + \left(\frac{\partial E}{\partial V} \right)_S dV$$

But comparison with the fundamental thermodynamic relation, which contains the physics, we can make the following identifications:

$$T = \left(\frac{\partial E}{\partial S} \right)_V \quad \text{and} \quad P = - \left(\frac{\partial E}{\partial V} \right)_S$$

These (especially the second) are interesting in their own right. But we can go further, by differentiating both sides of the first equation by V and of the second by S :

$$\left(\frac{\partial T}{\partial V} \right)_S = \left(\frac{\partial}{\partial V} \left(\frac{\partial E}{\partial S} \right)_V \right)_S \quad \text{and} \quad \left(\frac{\partial P}{\partial S} \right)_V = - \left(\frac{\partial}{\partial S} \left(\frac{\partial E}{\partial V} \right)_S \right)_V$$

Using the fact that the order of differentiation in the second derivation doesn't matter, we see that the right hand sides are equal, and thus so are the left hand sides, giving

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

By starting with F , H and G , we can get three more relations.

$dE = TdS - PdV \Rightarrow T = \left.\frac{\partial E}{\partial S}\right _V \quad \& \quad P = -\left.\frac{\partial E}{\partial V}\right _S$	\Rightarrow	$\left.\frac{\partial P}{\partial S}\right _V = -\left.\frac{\partial T}{\partial V}\right _S$
$dF = -SdT - PdV \Rightarrow S = -\left.\frac{\partial F}{\partial T}\right _V \quad \& \quad P = -\left.\frac{\partial F}{\partial V}\right _T$	\Rightarrow	$\left.\frac{\partial P}{\partial T}\right _V = \left.\frac{\partial S}{\partial V}\right _T$
$dH = TdS + VdP \Rightarrow T = \left.\frac{\partial H}{\partial S}\right _P \quad \& \quad V = \left.\frac{\partial H}{\partial P}\right _S$	\Rightarrow	$\left.\frac{\partial V}{\partial S}\right _P = \left.\frac{\partial T}{\partial P}\right _S$
$dG = -SdT + VdP \Rightarrow S = -\left.\frac{\partial G}{\partial T}\right _P \quad \& \quad V = \left.\frac{\partial G}{\partial P}\right _T$	\Rightarrow	$\left.\frac{\partial V}{\partial T}\right _P = -\left.\frac{\partial S}{\partial P}\right _T$

The two equations involving derivatives of S are particularly useful, as they provide a handle on S which isn't easily experimentally accessible.

For non-hydrodynamic systems, we can obtain analogous relations involving, say, m and B instead of P and V ; for instance by starting with $dE = TdS + mdB$ we get $(\partial T/\partial B)_S = (\partial m/\partial S)_B$.

To fully exploit these relations, some properties of partial derivatives are useful. See [here](#) for a refresher course!

In maths, it's usually quite obvious what the independent variables are: either x, y, z or r, θ, ϕ , for instance, and if you differentiate with respect to one you know that you are keeping the others constant. In thermal physics it isn't obvious at all, so **always** specify what is being held constant. Expressions like

$$\frac{\partial P}{\partial T} \quad \text{and} \quad \frac{dP}{dT}$$

are simply meaningless. (OK, we met the latter in the [Clausius-Clapeyron equation](#), but there it really was the slope of a line: the restriction to points of phase coexistence was understood.)

References

- Mandl 4.1,5
- Bowley and Sánchez 2.6 & E.2
- Adkins 7.3
- Zemansky 10.5

2.12.1 The rules of partial differentiation

- Identify the independent variables, eg u and v .
- If $w = w(u, v)$, the partial derivative of w with respect to u is obtained by holding v constant; it is written

$$\left(\frac{\partial w}{\partial u}\right)_v$$

- It follows that

$$\left(\frac{\partial v}{\partial u}\right)_v = \left(\frac{\partial u}{\partial v}\right)_u = 0 \quad \text{and} \quad \left(\frac{\partial u}{\partial u}\right)_v = \left(\frac{\partial v}{\partial v}\right)_u = 1$$

- The order of differentiation doesn't matter:

$$\left(\frac{\partial}{\partial v} \left(\frac{\partial w}{\partial u}\right)_v\right)_u = \left(\frac{\partial}{\partial u} \left(\frac{\partial w}{\partial v}\right)_u\right)_v$$

- The change in w as a result of changes in u and v is

$$dw = \left(\frac{\partial w}{\partial u}\right)_v du + \left(\frac{\partial w}{\partial v}\right)_u dv \quad (2.1)$$

- We could take v and w to be the independent variables, with $u = u(v, w)$. Now the partial derivatives are

$$\left(\frac{\partial u}{\partial v}\right)_w \quad \text{and} \quad \left(\frac{\partial u}{\partial w}\right)_v$$

Note the first is no longer required to be zero – it's w , not u , that is held constant. In this case,

$$du = \left(\frac{\partial u}{\partial v}\right)_w dv + \left(\frac{\partial u}{\partial w}\right)_v dw \quad (2.2)$$

- By comparing (2.1) and (2.2) with $dv = 0$, we see that

$$\left(\frac{\partial w}{\partial u}\right)_v = \frac{1}{\left(\frac{\partial u}{\partial w}\right)_v} \quad (2.3)$$

- From (2.1) we have

$$\begin{aligned} \left(\frac{\partial w}{\partial u}\right)_v du &= - \left(\frac{\partial w}{\partial v}\right)_u dv \quad \text{for constant } w \\ \Rightarrow \left(\frac{\partial w}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_w &= - \left(\frac{\partial w}{\partial v}\right)_u = - \left[\left(\frac{\partial v}{\partial w}\right)_u\right]^{-1} \quad \text{using (2.3)} \\ \Rightarrow \left(\frac{\partial w}{\partial u}\right)_v \left(\frac{\partial u}{\partial v}\right)_w \left(\frac{\partial v}{\partial w}\right)_u &= -1 \end{aligned}$$

In the second line, “dividing du by dv ” gave $\left(\frac{\partial u}{\partial v}\right)_w$, not $\frac{du}{dv}$, because the first line was only true for constant w .

- Rearranging (2.4) also gives

$$\left(\frac{\partial u}{\partial v}\right)_w = - \frac{\left(\frac{\partial w}{\partial v}\right)_u}{\left(\frac{\partial w}{\partial u}\right)_v} = - \frac{\left(\frac{\partial u}{\partial w}\right)_v}{\left(\frac{\partial v}{\partial w}\right)_u} \quad (2.5)$$

The minus sign in these is counter-intuitive.

Equations (2.3), (2.4) and (2.5) are our main results, and may be new to you.

References

- Bowley and Sánchez E.1

2.13 Heat Capacities

Take-home message: Heat capacities are related to changes of entropy with temperature.

A heat capacity C is the temperature change per unit heat absorbed by a system during a reversible process: $C dT = dQ^{\text{rev}}$. It is a poor name, since bodies don't contain heat, only energy, but we're stuck with it. (Note the difference between “heat capacity (C)” and “specific heat capacity (c)”; the latter is the heat capacity per kg or per mole - the units will make clear which.)

The heat capacity is different for different processes. Useful heat capacities are those at constant volume or constant pressure (for a fluid). Since

$$dQ^{\text{rev}} = TdS$$

we have at constant volume $C_V dT = TdS$, so

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V.$$

Similarly

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P.$$

Furthermore at constant volume, no work is done on the system and so $dQ^{\text{rev}} = dE$; hence

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V.$$

Also (usefully for chemists), at constant pressure $dQ^{\text{rev}} = dH$ where H is the [enthalpy](#), so

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P.$$

The **specific heat capacity** is the heat capacity per unit mass (or per mole). Heat capacities are not independent of temperature (or pressure) in general, but over a narrow temperature range they are often treated as such, especially for a solid.

Together with two of [Maxwell's relations](#), we now have expressions for the partial derivatives of the entropy with respect to all easily manipulable variables (P , V , T). These can be used to derive expressions for the entropy change in real processes. (see [here](#) for an example.)

We can also derive a relation between C_P , C_V , and other measurable properties of a substance which can be checked experimentally: if α is the isobaric thermal expansivity and κ_T is the isothermal compressibility

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Then we have the relation

$$C_P - C_V = VT \frac{\alpha^2}{\kappa_T}$$

which is always greater than zero. (The derivation is set as an exercise.) This relation is a firm prediction of thermal physics without any approximations whatsoever. It has to be true! For real gases and compressible liquids and solids it can be checked. For relatively incompressible liquids and solids it is hard to carry out processes at constant volume so C_V may not be well known and this equation can be used to predict it.

For one mole of a [van der Waals gas](#) this gives

$$C_P - C_V = R \left(1 - \frac{2a(V-b)^2}{RTV^3} \right)^{-1}.$$

In the ideal gas limit $a, b \rightarrow 0$ this reduces to $C_P - C_V = R$ as [expected](#).

References

- Mandl 5.3
- Bowley and Sánchez 2.5-6 & E.3
- Adkins 8.1
- Zemansky 10.6, 10.8

2.13.1 Entropy changes

What is the entropy change during the expansion of a [van der Waals gas](#) for which C_V is a constant?

The equation of state for one mole of a [van der Waals gas](#) is

$$P = \frac{RT}{V-b} - \frac{a}{V^2};$$

b represents the volume taken up by the finite size of the molecules, and a/V^2 is the reduction in pressure due to interactions between the molecules. In this way the two most important corrections neglected in the ideal gas are included. However the heat capacity at constant volume is still independent of temperature and volume, as in an ideal gas.

During an expansion, both the temperature and the volume may change. To calculate the change in entropy, we need

$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T}$$

and

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V-b}$$

so

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \quad \text{using a Maxwell relation} \\ &= \frac{C_V}{T} dT + \frac{R}{V-b} dV \end{aligned}$$

Note: Many problems on this section of the course involve choosing variables, either (T, V) or (T, P) , writing dS in terms of infinitesimal changes in these variables as in the first line, and

then using the definition of the heat capacities, and a Maxwell relation, to obtain something like the second line.

Then we can calculate the total entropy change by integrating, first at constant T and then at constant V :

$$\begin{aligned}
 S(T_1, V_2) &= S(T_1, V_1) + \int_{V_1}^{V_2} \left(\frac{\partial S(T_1, V)}{\partial V} \right)_T dV \\
 &= S(T_1, V_1) + \int_{V_1}^{V_2} \frac{R}{V-b} dV \\
 &= S(T_1, V_1) + R \ln \frac{V_2-b}{V_1-b} \\
 \text{and} \quad S(T_2, V_2) &= S(T_1, V_2) + \int_{T_1}^{T_2} \left(\frac{\partial S(T, V_2)}{\partial T} \right)_V dT \\
 &= S(T_1, V_2) + \int_{T_1}^{T_2} \frac{C_V}{T} dT \\
 &= S(T_1, V_2) + C_V \ln \frac{T_2}{T_1} \\
 &= S(T_1, V_1) + R \ln \frac{V_2-b}{V_1-b} + C_V \ln \frac{T_2}{T_1} \\
 \text{so} \quad S(T_2, V_2) - S(T_1, V_1) &= R \ln \frac{V_2-b}{V_1-b} + C_V \ln \frac{T_2}{T_1}
 \end{aligned}$$

where in the second integration we used the fact that C_V is constant. (We can do this integration because the two terms in dS are each functions of one variable only. Given that, the bottom line may be obvious to you without all the careful intermediate steps.)

Note that we have not said what kind of process (reversible or non-reversible, isothermal, adiabatic...) has taken place; that will go into the relation between V_2 and T_2 .

We can check our result against those we have already calculated for an ideal gas just by setting $b = 0$ and using the correct C_V (eg $3R/2$ for a monatomic gas), as follows: First, for an *isothermal* expansion ($T_1 = T_2$) we get $\Delta S = R \ln(V_2/V_1)$ as [before](#).

Also, for a *reversible adiabatic* expansion we can use $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ ([see here](#)) so

$$\begin{aligned}
 \Delta S &= R \ln \frac{V_2}{V_1} + C_V \ln \left(\frac{V_1}{V_2} \right)^{\gamma-1} \\
 &= \left(R - C_V \left(\frac{C_P}{C_V} - 1 \right) \right) \ln \frac{V_2}{V_1} \\
 &= 0
 \end{aligned}$$

(using $C_P - C_V = R$ for an [ideal gas](#)). But that is as expected: entropy changes for reversible, adiabatic processes are it always zero! (See [here](#) if you have forgotten why...)

Conversely, we can use the fact that $\Delta S = 0$ for a reversible adiabatic process to see that for a van der Waals gas, $T(V-b)^{R/C_V}$ is constant. But $R \neq C_P - C_V$ so the exponent isn't $\gamma - 1$.

2.14 Joule-Thomson Expansion

Several times, we have noted that the free adiabatic expansion of an ideal gas does not result in a change of temperature; this is because the energy depends only on the temperature and

not on the volume, so if the internal energy is unchanged, so is the temperature. This is not true for a real gas though. In general a free expansion will result in cooling as internal work is done against the forces of attraction between the molecules. More formally

$$\left(\frac{\partial T}{\partial V}\right)_E = -\left(\frac{\partial E}{\partial V}\right)_T \bigg/ \left(\frac{\partial E}{\partial T}\right)_V = -\frac{1}{C_V} \left(T \left(\frac{\partial P}{\partial T}\right)_V - P\right)$$

where we have used the FTR and a Maxwell relation in the last step. For an ideal gas this is zero, but for a van der Waal gas, it gives

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{1}{c_v} \frac{a}{V^2} < 0.$$

Something like this can be used to cool gases to low temperatures, but the process is a little more complicated. For practical purposes we want a continuous flow of coolant which passes through a throttle from a region of higher to lower pressure. If we consider a certain amount

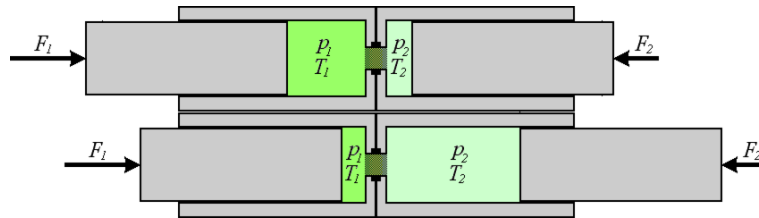


Figure 2.1: Schematic diagram of the throttling process, considering a certain mass of gas.

of gas, starting at (V_1, P_1, T_1) and ending after passing through the throttle at (V_2, P_2, T_2) , with no heat flow, the energy change is due only to the work done by the pressures on either side, so

$$E_2 - E_1 = P_1 V_1 - P_2 V_2 \quad \Rightarrow \quad H_1 = H_2$$

In other words, the continuous-flow throttling process is isenthalpic (constant enthalpy). Now the rate of change of temperature with pressure, which should be positive if cooling is to occur as the pressure falls, is

$$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \bigg/ \left(\frac{\partial H}{\partial T}\right)_P = \frac{1}{C_P} \left(T \left(\frac{\partial V}{\partial T}\right)_P - V\right)$$

This can be positive or negative, as can be seen from the lines of constant enthalpy on the plot above. The line on which the slope vanishes is called the inversion curve, and cooling will only take place if we start at temperatures and pressures to the left of it. The inversion curve intersects the T axis at a temperature T_i above which no cooling can occur, so pre-cooling may be necessary e.g. for hydrogen. In the plot, if we start at point A and lower the pressure, we can end up at the cooler, lower-pressure point B.

This effect, with recycling of the cooled gas to obtain further cooling, was pioneered by James Joule and William Thomson (later Lord Kelvin) in Salford in 1852, and formed the basis for the first successful liquefaction of oxygen and carbon monoxide in 1877 by Louis Cailletet. See an interesting discussion by “[Carnocycle](#)”.

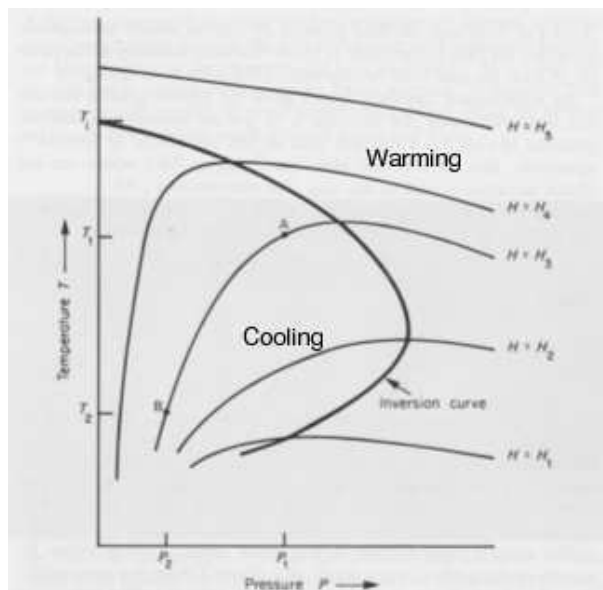


Figure 2.2: Isenthals and the inversion curve for a typical gas. Figure taken from Mandl

2.15 Systems with more than one component

Take-home message: The chemical potential is important wherever the number of molecules in a system isn't fixed.

If we have a mixture of two substances present, the internal energy and all the other thermodynamical potentials will depend on how much of each is present, since there will be interactions between the molecules of each.

Here we focus on the Gibbs free energy, since the relevant conditions are usually those of fixed temperature and pressure.

We have $G = G(T, P, N_1, N_2)$ where N_1 and N_2 are the number of molecules of each substance. (This is easily generalised more than two components.) So

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, N_1, N_2} dT + \left(\frac{\partial G}{\partial P} \right)_{T, N_1, N_2} dP + \left(\frac{\partial G}{\partial N_1} \right)_{T, P, N_2} dN_1 + \left(\frac{\partial G}{\partial N_2} \right)_{T, P, N_1} dN_2$$

Now the first two partial derivatives are $-S$ and V as before. We *define*

$$\mu_1 = \left(\frac{\partial G}{\partial N_1} \right)_{T, P, N_2} \quad \text{and} \quad \mu_2 = \left(\frac{\partial G}{\partial N_2} \right)_{T, P, N_1}$$

giving

$$dG = -SdT + VdP + \mu_1 dN_1 + \mu_2 dN_2$$

μ_1 is called the **chemical potential** of substance 1. But what is its significance?

First, imagine only **one** substance present. Then

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

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.

But for a two component system, G depends not only on the extensive variable $N_1 + N_2$ 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. All we can say is μ_1 is the *extra* Gibbs free energy per added molecule of substance 1. If substance 1 is ethanol and substance 2 water, the chemical potential of ethanol is different in beer (5%) and vodka (40%).

However for ideal gases, since there are no intermolecular interactions, the Gibbs free energies are independent and additive: $G = \mu_1 N_1 + \mu_2 N_2$.

From $E = G - PV + TS$, $F = G - PV$ and $H = G + TS$ ([see here](#)), we see that the term $\mu_1 dN_1 + \mu_2 dN_2$ is added to dE , dF and dH also, and

$$\mu_1 = \left(\frac{\partial E}{\partial N_1} \right)_{S,V,N_2} = \left(\frac{\partial F}{\partial N_1} \right)_{T,V,N_2} = \left(\frac{\partial H}{\partial N_1} \right)_{S,P,N_2}.$$

An important use of chemical potentials is in [chemical reactions](#). But it is important to physicists too. Not all reactions are chemical: in a neutron star, neutrons, protons and electrons can interact via $p + e^- \rightleftharpoons n$; 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. (Why? I'm afraid that must wait till next year!)

The chemical potential also governs systems which can exchange particles with a reservoir, and that is the context in which we will meet it in statistical physics.

Note: the use of μ to mean magnetic moment as well as chemical potential should never confuse, as magnets tend to have fixed numbers of atoms.

If like most students you find the chemical potential mystifying, look at [this](#) helpful slide from Peter Saeta of Harvey Mudd College. The last point will only become clear once we've done Gibbs distributions at the end of the course.

References

- Mandl 8.1
- Bowley and Sánchez 2.9
- Adkins 11.3
- Zemansky 11.6

2.16 Chemical reactions

Take-home message: At equilibrium the chemical potential of reactants and products are equal.

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 thirty years).

2.16.1 More on chemical equilibrium

In general the chemical potential of species A will depend on the number of molecules of all species present. However things simplify tremendously if we have a gaseous reaction and all species can be treated as ideal gases at these temperatures and pressures. For a single ideal gas we have

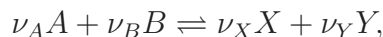
$$S(T, P) = S(T_0, P_0) + C_P \ln \frac{T}{T_0} - nR \ln \frac{P}{P_0}.$$

The Gibbs free energy is defined for an ideal gas as $G = E - TS + PV = E(T) - TS + nRT$. Hence for one mole at constant temperature T_0 ,

$$g(P, T_0) - g(P_0, T_0) = -T_0(S(T_0, P) - S(T_0, P_0)) = RT_0 \ln \frac{P}{P_0}.$$

Recall that in a mixture, the relevant pressure is the partial pressure of the species in question.

So for a reaction in which ν_A moles of A and ν_B moles of B react to form ν_X moles of X and ν_Y moles of Y,



we define the Gibbs free energy of reaction as

$$g_r = \nu_X g_X + \nu_Y g_Y - \nu_A g_A - \nu_B g_B$$

and this will be zero at equilibrium. (Recall μ and g are the same for ideal gases.)

If we know this quantity g_r at some reference temperature and pressure, the same for all reactants and products, usually 25°C and 1 atm, call it g_r^0 , then at other partial pressures but the same temperature it will be

$$g_r(P_X, P_A, T_0) = g_r^0 + RT_0 \left(\nu_X \ln \frac{P_X}{P_0} + \nu_Y \ln \frac{P_Y}{P_0} - \nu_A \ln \frac{P_A}{P_0} - \nu_B \ln \frac{P_B}{P_0} \right) = RT_0 \ln \left[\left(\frac{P_X}{P_0} \right)^{\nu_X} \left(\frac{P_Y}{P_0} \right)^{\nu_Y} \left(\frac{P_0}{P_A} \right)^{\nu_A} \right]$$

Hence, since at equilibrium $g_r = 0$,

$$\left(\frac{P_X}{P_0} \right)^{\nu_X} \left(\frac{P_Y}{P_0} \right)^{\nu_Y} \left(\frac{P_0}{P_A} \right)^{\nu_A} \left(\frac{P_0}{P_B} \right)^{\nu_B} = \exp \left(-\frac{g_r^0}{RT_0} \right).$$

If at standard pressure and temperature $g_r^0 < 0$, the reaction will tend to increase the amount of the products (X, Y) and decrease the amount of the reactants (A, B); if on the other hand $g_r^0 > 0$ the reaction will proceed in the other direction.

The general forms of these equations for N reactants and N' products can be written

$$g_r = \sum_{i=1}^{N'} \nu_{X_i} g_{X_i} - \sum_{j=1}^N \nu_{A_j} g_{A_j}$$

and, at equilibrium,

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

As given, g_r will depend on whether the reaction is written, e.g., $\text{O}_2 + 2\text{H}_2 \rightleftharpoons 2\text{H}_2\text{O}$ or $\frac{1}{2}\text{O}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O}$, 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.

Chapter 3

The statistical theory of thermodynamics

The classical theory of thermodynamics leaves certain questions unanswered:

- What really is entropy?
- Why does entropy increase?
- Can we deduce equations of state from first principles?

The statistical theory can answer all these.

3.1 Microstates and Macrostates

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

Classical thermodynamics describes **macroscopic** systems in terms of a few variables (**functions of state**): temperature, pressure, volume... But such a system is really made of atoms, so a much richer description must be possible in principle: we could specify the quantum state of all the atoms—the **microstate**. Of course as the atoms interact this state changes very rapidly—perhaps 10^{35} times a second. But the observed **macrostate** doesn't change. Many different microstates all correspond to the same macrostate.

This suggests we can calculate the macroscopic behaviour of the system by averaging over the corresponding microstates. We can derive thermodynamics from the quantum behaviour of atoms and molecules.

Of course only a few systems are really fully calculable: those in which the interactions between atoms are particularly simple—or absent. We will be able to tackle the ideal paramagnet and the ideal gas, including the latter at densities so high that the quantum nature of the system becomes important. The van der Waals gas and a paramagnet with nearest neighbour interactions can be worked out, as can crystalline solids with simple defects. Going beyond that is tough. But the proof-of-principle that these give is compelling.

The crucial link from microscopic to macroscopic properties is as follows. If the value of some quantity X in the i th 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** (more details [here](#).)

$$\langle X \rangle = \sum_i p_i X_i$$

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 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

$$p_i = \frac{1}{\Omega} \quad \text{and} \quad \sum_i p_i = \Omega \frac{1}{\Omega} = 1$$

The idea of microstates is explored in a simple example [here](#).

References

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

3.1.1 Ensembles

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,

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

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**.

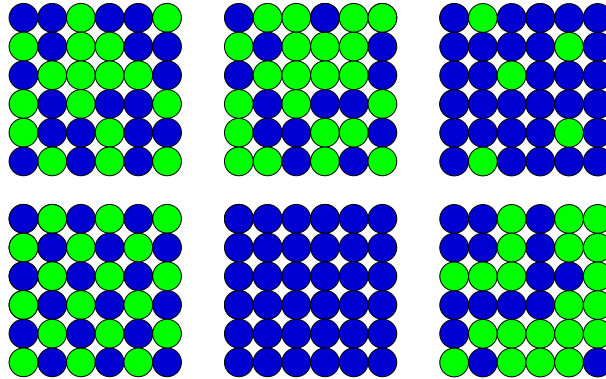
If the real system is in contact with a **heat bath**, that is at fixed **temperature**, the copies are assumed to be in thermal contact, with all the rest of the copies acting as a heat bath of any individual copy. This is called the **canonical ensemble**.

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**.

3.1.2 Microstates

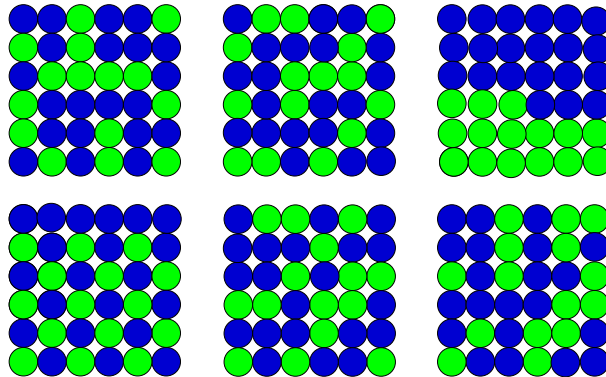
Imagine we have counters, blue on one side and green on the other, and we toss them and place them on a 6×6 checkerboard. Full information involves listing the colour at each site: this is the equivalent of a microstate.

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 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 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 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

$$\frac{N!}{n!(N-n)!}$$

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.

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.

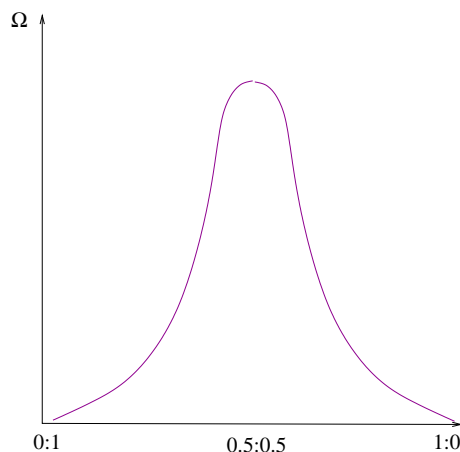
The numbers $N!/n!(N-n)!$ are called the *binomial coefficients* (since they enter the binomial expansion) and they are written ${}^N C_n$ or $\binom{N}{n}$.

3.2 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. (See [here](#) for a calculation of the entropy change). 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: 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 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

$$S = k_B \ln \Omega$$

then we can understand both entropy and its increase.

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:

$$k_B = \frac{R}{N_A} = 1.381 \times 10^{-23} \text{J K}^{-1} = 8.617 \times 10^{-5} \text{eV K}^{-1}$$

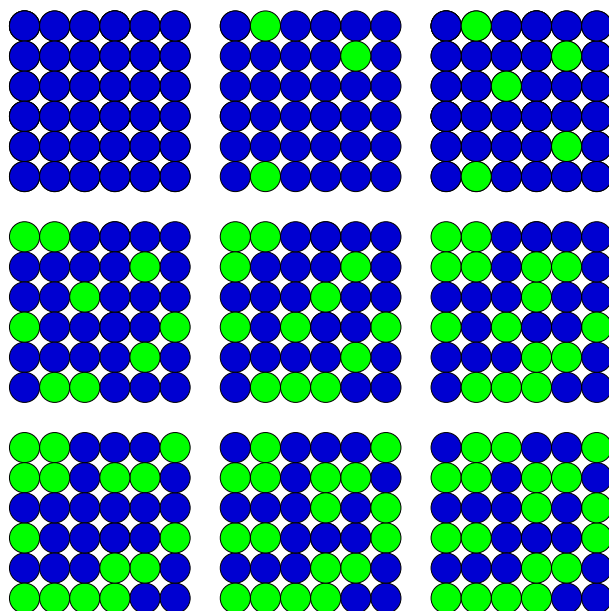
Find a simple example of these ideas [here](#).

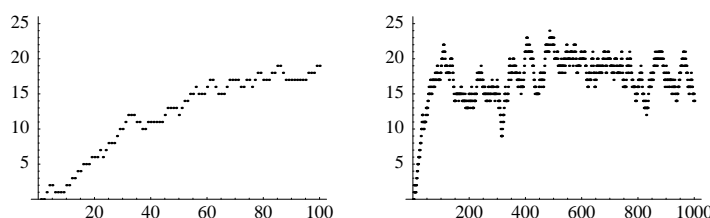
References

- Mandl 2.3
- Bowley and Sánchez 4.5
- Kittel and Kroemer 1,2

3.2.1 Equilibrium on the checkerboard

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.

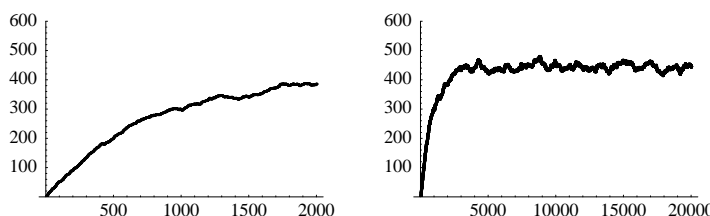




Here is a graph of the number of greens over 100 and 1000 moves.

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.

3.3 The spin-half paramagnet

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

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

$$m = n_\uparrow\mu + n_\downarrow(-\mu) = \mu(2n_\uparrow - N).$$

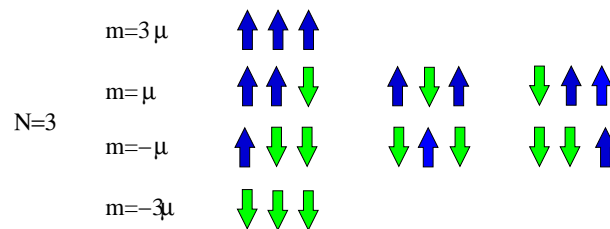
In an external field, the spin-up atoms will have lower energy, $-\mu B$, and the spin-down atoms have higher energy, μB , so the the total energy is just

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

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](#).

If you haven't already looked at the chequerboard examples, [here](#) and [here](#), do so now. 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 nine microstates. In general the number of microstates for a given macrostate, with $n_{\uparrow} =$

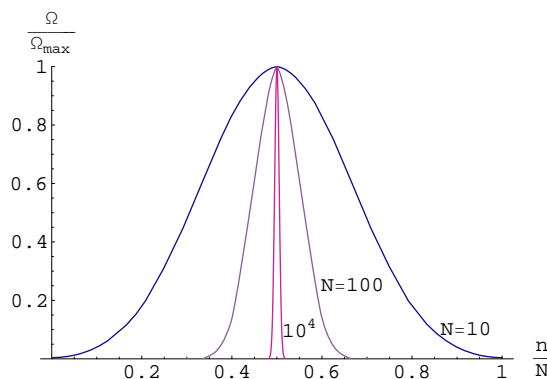


$\frac{1}{2}(N + m/\mu)$, is

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

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

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,

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

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

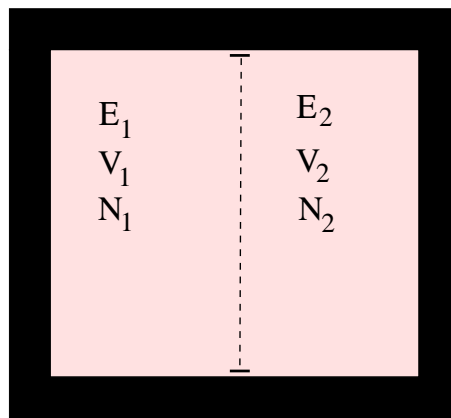
Since the probabilities of various sizes of fluctuations from the mean in a Gaussian are known, we can show that in a macroscopic system, 100σ deviations are vanishingly unlikely. Even they would be undetectable, so the macroscopic magnetisation is very well defined indeed.

References

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

3.4 From entropy to temperature

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



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.

Clearly these are related to the usual concepts of temperature, pressure and chemical potential. The correct relations are the ones which reproduce the [fundamental thermodynamic relation](#)

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN,$$

namely

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

[Details](#) of the derivation are given here.

As an example, these ideas are applied to the paramagnet [here](#). We can have our first go at the ideal gas now, too; see [here](#).

References

- Mandl 2.4
- (Bowley and Sánchez 2.9)

3.4.1 Deriving temperature etc

We can derive the ideas of temperature, pressure and chemical potential from the entropy. 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,

$$dS = \left(\frac{\partial S}{\partial E_1} \right)_{V,N} dE_1 + \text{chemical} \left(\frac{\partial S}{\partial E_2} \right)_{V,N} dE_2$$

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

$$S(E_1, E_2, V_1, V_2, N_1, N_2) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

and also, since the total energy is conserved, $dE_1 = -dE_2$. So

$$dS = \left[\left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} - \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} \right] dE_1$$

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

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

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:

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

since they give

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

which is the [fundamental thermodynamic relation](#) rearranged.

3.4.2 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 $-PdV$ we have $-m dB$ in the fundamental thermodynamic relation, so we have an expression for m instead of P :

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

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

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

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

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

$$\ln n! = n \ln n - n$$

giving

$$S = k_B (N \ln N - n_{\uparrow} \ln n_{\uparrow} - (N - n_{\uparrow}) \ln(N - n_{\uparrow})).$$

(Note that S is maximum, $S = N k_B \ln 2$, when $n_{\uparrow} = n_{\downarrow} = N/2$, the point of maximum disorder. This is the expected value, as at this point $\Omega = 2^N$)

So

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

There will always be more spins aligned with the field than against it, so T is positive.

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

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

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

3.4.3 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 PC210 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

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

and

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

So we have derived the ideal gas equation!

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 4

Statistical Physics of Non-isolated Systems

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.

4.1 The Boltzmann Distribution

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

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

$$p_i = \frac{e^{-\varepsilon_i/k_B T}}{Z}$$

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

$$Z = \sum_j e^{-\varepsilon_j/k_B T}$$

The details of the derivation are [here](#). In outline, we consider the system S and heat reservoir R together as a larger, isolated system with a total energy which is fixed but which can be differently distributed between its two parts. If we specify the microstate (and 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 particle can be considered as the system S and all the others form the reservoir R . 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

$$p_{\uparrow} = \frac{e^{\mu B/k_B T}}{Z_1}$$

$$p_{\downarrow} = \frac{e^{-\mu B/k_B T}}{Z_1}$$

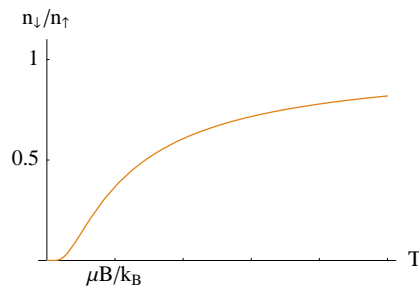
and $Z_1 = e^{\mu B/k_B T} + e^{-\mu B/k_B T}$

(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 $\langle n \rangle_{\uparrow} = N p_{\uparrow}$, so we have

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

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).



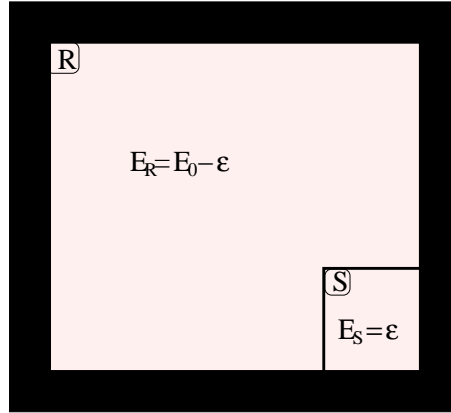
Note that in thermal equilibrium, the average number of particles in the higher energy state is *always* less than the number in the lower energy state. As the temperature tends to infinity the ratio approaches, but never exceeds, one.

References

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

4.1.1 Derivation of the Boltzmann distribution

We consider a system S in contact with a heat reservoir R , the whole forming an isolated system with energy E_0 .



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 i th (with energy ε_i) and ask what the probability p_i of finding the system in that microstate is. It will be proportional to the number of 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 $\Omega(E_0, \varepsilon_i) = \Omega_R(E_0 - \varepsilon_i)$

Using the [relation](#) between Ω and entropy, we can write

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

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:

$$S_R(E_0 - \varepsilon_i) = S_R(E_0) - \varepsilon_i \left(\frac{\partial S_R}{\partial E} \right)_{V,N} + \dots$$

But the derivative of S with respect to E is just the inverse of the temperature, so we have

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

(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:

$$p_i = \frac{e^{-\varepsilon_i/k_B T}}{Z}$$

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

$$Z = \sum_j e^{-\varepsilon_j/k_B T}$$

4.2 The Partition Function

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:

$$Z = \sum_j e^{-\varepsilon_j/k_B T}$$

where the sum is over all the microstates of the system.

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

$$\langle E \rangle = \sum_i \varepsilon_i p_i = \frac{\sum_i \varepsilon_i e^{-\varepsilon_i/k_B T}}{\sum_j e^{-\varepsilon_j/k_B T}}$$

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 “ $1/(k_B T)$ ”. This is a bit awkward, so we introduce a new symbol

$$\beta \equiv \frac{1}{k_B T}$$

giving

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

or

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

(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.)

From the energy we can find the heat capacity:

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

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

$$(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2$$

It can be [shown](#) that $(\Delta E)^2$ is related to the heat capacity,

$$(\Delta E)^2 = (k_B T)^2 \frac{C_V}{k_B}$$

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

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

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.

References

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

4.2.1 Fluctuations

To derive $(\Delta E)^2 = (k_B T)^2 C_V / k_B$ the following intermediate steps are useful:

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

(should be obvious by analogy with the corresponding expression for $\langle E \rangle$) and hence

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

In the main text we said that for “normal” macroscopic systems the fluctuations were unobservable. 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. Nice pictures can be found [here](#) courtesy of M. de Podesta of UCL, together with further explanation [here](#).

4.3 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.

Here is the crucial equation which links the Helmholtz free energy and the partition function:

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

The details of the derivation can be found [here](#).

Since $F = E - TS$, from the [fundamental thermodynamic relation](#) we obtain $dF = -SdT - PdV + \mu dN$. Thus

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

(We first met these in the derivation of [Maxwell's relations](#).) For a magnetic system, we have $m = -(\partial F / \partial B)_{T,N}$ 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:

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

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](#).)

References

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

4.3.1 Entropy in a non-isolated system

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 i th microstate, so the number of ways of arranging these is

$$\Omega_\nu = \frac{\nu!}{\nu_1! \nu_2! \nu_3! \dots}$$

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

So, using Stirling's approximation,

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

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

$$\langle S \rangle = -k_B \sum_i p_i \ln p_i$$

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 $S = k_B \ln \Omega$ as before.

For a system in contact with a heat bath, p_i is given by the Boltzmann distribution, so

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

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

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

4.4 The paramagnet at fixed temperature

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

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

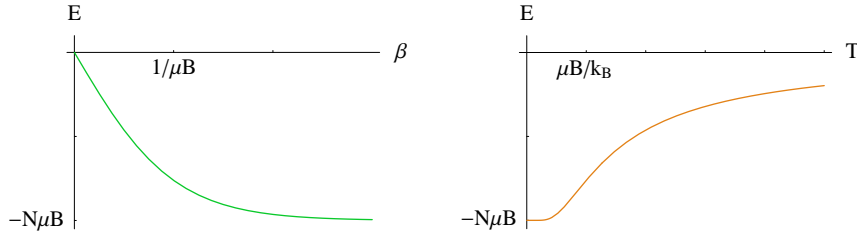
$$Z_1 = e^{\mu B/k_B T} + e^{-\mu B/k_B T} = 2 \cosh \left(\frac{\mu B}{k_B T} \right) = 2 \cosh (\mu B \beta)$$

(Remember $\beta = 1/k_B T$.)

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

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

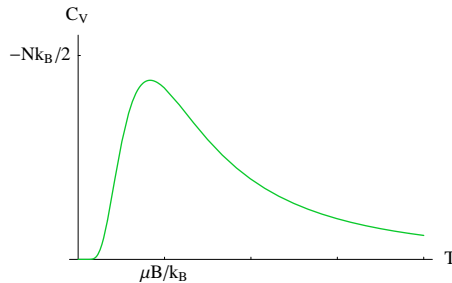
(For a refresher on hyperbolic trig functions, see [here](#).)



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 $k_B T$ 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**, $\langle n_{\downarrow}/n_{\uparrow} \rangle = \exp(-2\mu B/k_B T)$, so it never exceeds one.

We can also calculate the heat capacity :

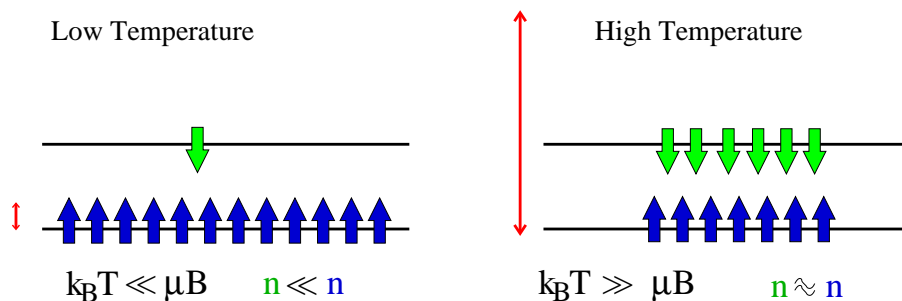
$$C_V = \frac{\partial E}{\partial T} = N k_B (\mu B \beta)^2 \text{sech}^2(\mu B \beta)$$



We see that the heat capacity tends to zero both at high and low T . At low T the heat capacity is small because $k_B T$ 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.

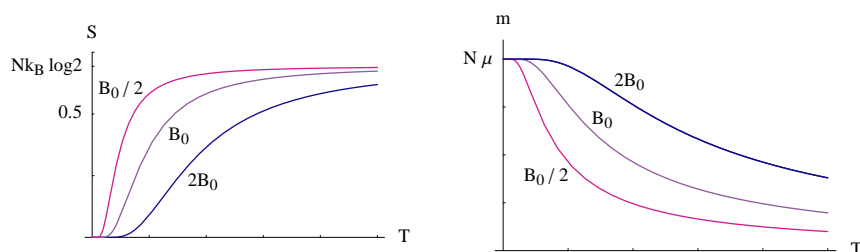
Up to now we've cheated a bit, (though the results are correct,) in that we didn't calculate the partition function for the whole system, only for a single spin. It is easy to show however that the partition function for N non-interacting spins on a lattice is



$$Z_N = (Z_1)^N$$

(Details and a caveat [here](#).) 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. We can also calculate the Helmholtz free energy, $F = -k_B T \ln Z_N$, and the entropy, from $S = -(\partial F / \partial T)_{B,N}$ or from $S = (E - F)/T$. We can also calculate the magnetisation, $m = -(\partial F / \partial B)_{T,N}$ and find that $m = -E/B$ as expected.

Below we plot S and m against temperature for several different external fields. (For details of the algebra behind the plots see [here](#).) 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](#).

References

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

4.4.1 The N -particle partition function for distinguishable particles

Let's start with two spins. There are four states of the whole system, $\uparrow\uparrow$ with energy $-2\mu B$, $\uparrow\downarrow$ and $\downarrow\uparrow$, both with energy zero, and $\downarrow\downarrow$ with energy $2\mu B$. Thus the two-particle partition

function is

$$\begin{aligned} Z_2 &= e^{2\mu B\beta} + e^0 + e^0 + e^{-2\mu B\beta} = e^{2\mu B\beta} + 2 + e^{-2\mu B\beta} \\ &= (e^{\mu B\beta} + e^{-\mu B\beta})^2 = (Z_1)^2 \end{aligned}$$

In general, for N particles, the energies range through $-N\mu B, -(N-2)\mu B, \dots, -(N-2n_\downarrow)\mu B, \dots, N\mu B$ with there being $N!/n_\downarrow!(N-n_\downarrow)!$ separate states with n_\downarrow down-spins. So

$$\begin{aligned} Z_N &= e^{-N\mu B\beta} + \dots + \frac{N!}{n_\downarrow!(N-n_\downarrow)!} e^{-(N-2n_\downarrow)\mu B\beta} + \dots + e^{N\mu B\beta} \\ &= (e^{-\mu B\beta} + e^{\mu B\beta})^N = (Z_1)^N \end{aligned}$$

There is a caveat, which can be ignored on first reading. The argument says that there are a number of different states with the same number of 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](#).

4.4.2 Details of the paramagnet calculation

The starting point is the Boltzmann probabilities for the two energy states of a single spin, $\varepsilon_\uparrow = -\mu B$ and $\varepsilon_\downarrow = \mu B$:

$$\begin{aligned} p_\uparrow &= \frac{e^{\mu B/k_B T}}{Z_1} \\ p_\downarrow &= \frac{e^{-\mu B/k_B T}}{Z_1} \\ \text{and } Z_1 &= e^{\mu B/k_B T} + e^{-\mu B/k_B T} = 2\cosh(\mu B\beta) \end{aligned}$$

In this simple case both the average energy and magnetisation of a single spin can be found directly from the probabilities:

$$\begin{aligned} \langle E_1 \rangle &= \varepsilon_\uparrow p_\uparrow + \varepsilon_\downarrow p_\downarrow \\ &= -\mu B \frac{e^{\mu B/k_B T}}{Z_1} + \mu B \frac{e^{-\mu B/k_B T}}{Z_1} \\ &= -\mu B \frac{e^{\mu B/k_B T} - e^{-\mu B/k_B T}}{e^{\mu B/k_B T} + e^{-\mu B/k_B T}} \\ &= -\mu B \tanh(\mu B/k_B T) = -\mu B \tanh(\mu B\beta) \quad (\text{using } \beta = 1/k_B T) \end{aligned}$$

and similarly

$$\begin{aligned} \langle m_1 \rangle &= (+\mu)p_\uparrow + (-\mu)p_\downarrow \\ &= \mu \tanh(\mu B\beta) \end{aligned}$$

But for things like the entropy which only makes sense for the whole system, and as a warm-up for more complicated cases, we can use the partition function method instead; the results for the energy and magnetisation are the same.

We also have

$$\langle F \rangle = -k_B T \ln \left[(2 \cosh(\mu B \beta))^N \right] = -N k_B T \ln (2 \cosh(\mu B \beta))$$

and

$$\begin{aligned} \langle S \rangle &= - \left(\frac{\partial \langle F \rangle}{\partial T} \right)_{B,N} \\ &= N k_B \ln (2 \cosh(\mu B \beta)) + N k_B T \frac{d\beta}{dT} \left(\frac{\partial \ln (2 \cosh(\mu B \beta))}{\partial \beta} \right)_{B,N} \\ &= N k_B \ln (2 \cosh(\mu B \beta)) - N k_B T \frac{1}{k_B T^2} \mu B \tanh(\mu B \beta) \\ &= N k_B \{ \ln (2 \cosh(\mu B \beta)) - \mu B \beta \tanh(\mu B \beta) \} \end{aligned}$$

which does indeed equal $(E - F)/T$.

4.4.3 Hyperbolic Trigonometry

Remember that ordinary trig functions are defined as follows:

$$\cos \theta = \frac{1}{2}(e^{i\theta} + e^{-i\theta}) \quad \sin \theta = \frac{1}{2i}(e^{i\theta} - e^{-i\theta})$$

and it is useful sometimes to use the extra functions

$$\sec \theta \equiv \frac{1}{\cos \theta} \quad \operatorname{cosec} \theta \equiv \frac{1}{\sin \theta} \quad \cot \theta \equiv \frac{1}{\tan \theta}$$

Hyperbolic trig functions are defined similarly:

$$\begin{aligned} \cosh x &= \frac{1}{2}(e^x + e^{-x}) & \sinh x &= \frac{1}{2}(e^x - e^{-x}) \\ \operatorname{sech} x &\equiv \frac{1}{\cosh x} & \operatorname{cosech} x &\equiv \frac{1}{\sinh x} & \coth x &\equiv \frac{1}{\tanh x} \end{aligned}$$

From the definitions above it is easy to show that

$$\frac{d \cosh x}{dx} = \sinh x \quad \frac{d \sinh x}{dx} = \cosh x \quad \frac{d \tanh x}{dx} = \operatorname{sech}^2 x.$$

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 $x \rightarrow 0$, $\sinh x \rightarrow 0$, that is not usually what we want; what we want is *how* it tends to zero.

From the small- x expansion of the exponential $e^x = 1 + x + \frac{1}{2}x^2 + \dots$ we get

$$\sinh x \xrightarrow{x \rightarrow 0} x \quad \tanh x \xrightarrow{x \rightarrow 0} x \quad \cosh x \xrightarrow{x \rightarrow 0} 1 + \frac{1}{2}x^2$$

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

$$\cosh x \xrightarrow{x \rightarrow 0} 1 \quad \text{but} \quad \cosh x - 1 \xrightarrow{x \rightarrow 0} \frac{1}{2}x^2$$

The same is true of the exponential:

$$e^x \xrightarrow{x \rightarrow 0} 1 \quad \text{but} \quad e^x - 1 \xrightarrow{x \rightarrow 0} x.$$

In a particular problem we find that the energy of a system is

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

Naively we would say that at high temperatures, as $\beta \rightarrow 0$, 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 $\langle E \rangle \rightarrow 1/\beta = k_B T$. That is a much more useful prediction, since it can be verified experimentally.

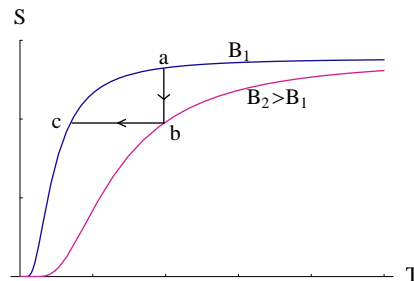
The high- x limits are easier; $e^{-x} \rightarrow 0$ and so

$$\sinh x \xrightarrow{x \rightarrow \infty} \frac{1}{2}e^x \quad \cosh x \xrightarrow{x \rightarrow \infty} \frac{1}{2}e^x \quad \tanh x \xrightarrow{x \rightarrow \infty} 1$$

4.5 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.

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



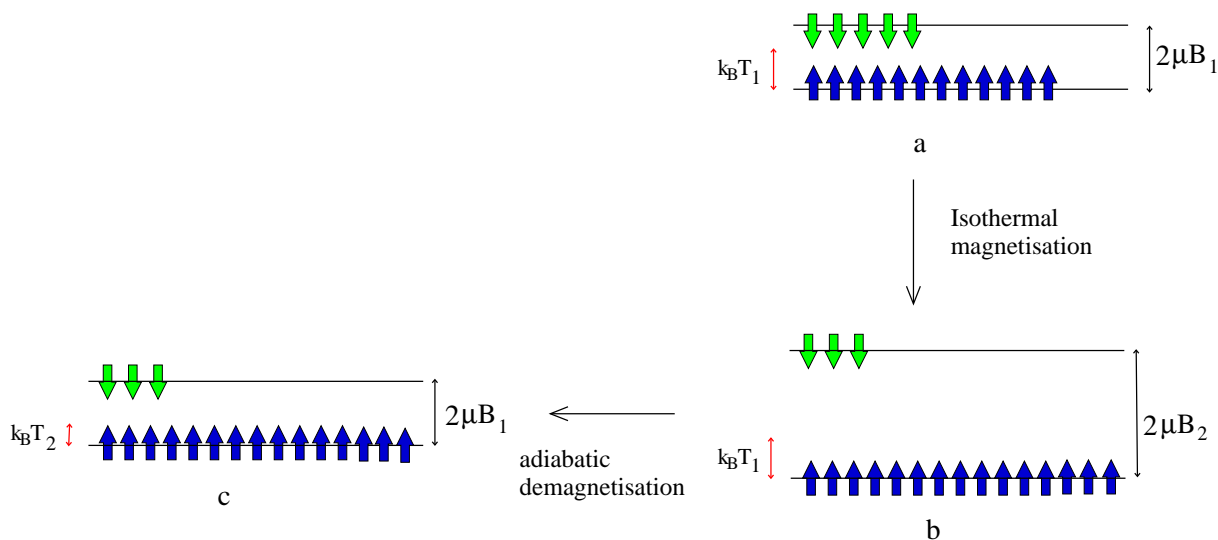
We start with the sample in a magnetic field B_1 at an (already fairly low) temperature T_1 .

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

b \rightarrow 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 $T \rightarrow 0$. (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. (Wondering why we can't just take B_1 to zero? See [here](#) for the real paramagnet.)

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

The laws of Thermodynamics

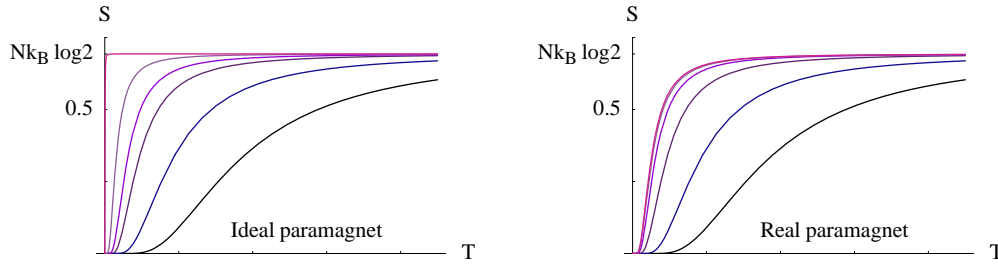
- 1: You can't win, you can only break even.
- 2: You can only break even at $T=0$.
- 3: You can't reach $T=0$

References

- Mandl 5.6

4.5.1 The real paramagnet

In the process above, the lowest temperature attainable is obviously proportional to $\mu B_1 / k_B$. In the ideal paramagnet, as B is reduced the graph of S against T rises more and more steeply, going to a step function at $B = 0$. 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.



4.6 Vibrational and rotational energy of a diatomic molecule

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

$$\varepsilon_n = (n + \frac{1}{2})\hbar\omega \quad n = 0, 1, 2 \dots$$

so

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

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

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

The low temperature limit of this ($k_B T \ll \hbar\omega$; $\hbar\omega\beta \rightarrow \infty$) is $\frac{1}{2}\hbar\omega$, which is what we expect if only the ground state is populated. The high temperature limit ($k_B T \gg \hbar\omega$; $\hbar\omega\beta \rightarrow 0$) 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

$$\varepsilon_l = \frac{l(l+1)\hbar^2}{2\mathcal{I}} \quad l = 0, 1, 2 \dots$$

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

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

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, ($k_B T \gg \hbar^2/2\mathcal{I}$) 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

$$Z_1 = \frac{\mathcal{I}}{\hbar^2 \beta}$$

$$\langle E_1 \rangle = k_B T$$

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 $k_B T$ in both cases! These are examples of **equipartition** which is the subject of a future [section](#).

References

- (Bowley and Sánchez 5.11,5.12)

4.7 Translational energy of a molecule in an ideal gas

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 $V \equiv L_x L_y L_z$. The sides of the box are impenetrable, so the wavefunction ψ must vanish there, but inside the box the atom is free and so ψ satisfies the free Schrödinger equation

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

The equation, and the boundary conditions, are satisfied by

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

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

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

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

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

In general this cannot be further simplified. However there can be simplifications if $k_B T$ 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 $\hbar^2 \pi^2 / 2m L^2 \approx 10^{-20}$ 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. We choose k_x , k_y and k_z as the variables, and replace \sum_{n_x} with $(L_x/\pi) \int dk_x$, giving

$$\begin{aligned}
Z_1 &= \frac{L_x L_y L_z}{\pi^3} \int_0^\infty \int_0^\infty \int_0^\infty dk_x dk_y dk_z e^{-\varepsilon(k)\beta} \\
&= \frac{V}{\pi^3} \int_0^\infty \int_0^{\pi/2} \int_0^{\pi/2} k^2 \sin \theta_k dk d\theta_k d\phi_k e^{-\varepsilon(k)\beta} \quad \text{converting to spherical polar coordinates} \\
&= \frac{1}{8} 4\pi \frac{V}{\pi^3} \int_0^\infty k^2 dk e^{-\varepsilon(k)\beta} \\
&\equiv \int_0^\infty D(k) e^{-\varepsilon(k)\beta} dk \quad \text{where } D(k) \equiv V k^2 / 2\pi^2
\end{aligned}$$

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. $D(k)$ is called the “density of states” in k -space; $D(k)dk$ is the number of states within range of $k \rightarrow k + dk$. 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:

$$\begin{aligned}
Z_1 &= \frac{V}{2\pi^2} \int_0^\infty k^2 dk e^{-\hbar^2 k^2 \beta / 2m} \\
&= V \left(\frac{m}{2\pi \hbar^2 \beta} \right)^{3/2} \equiv V n_Q.
\end{aligned}$$

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:

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

as we should have expected.

References

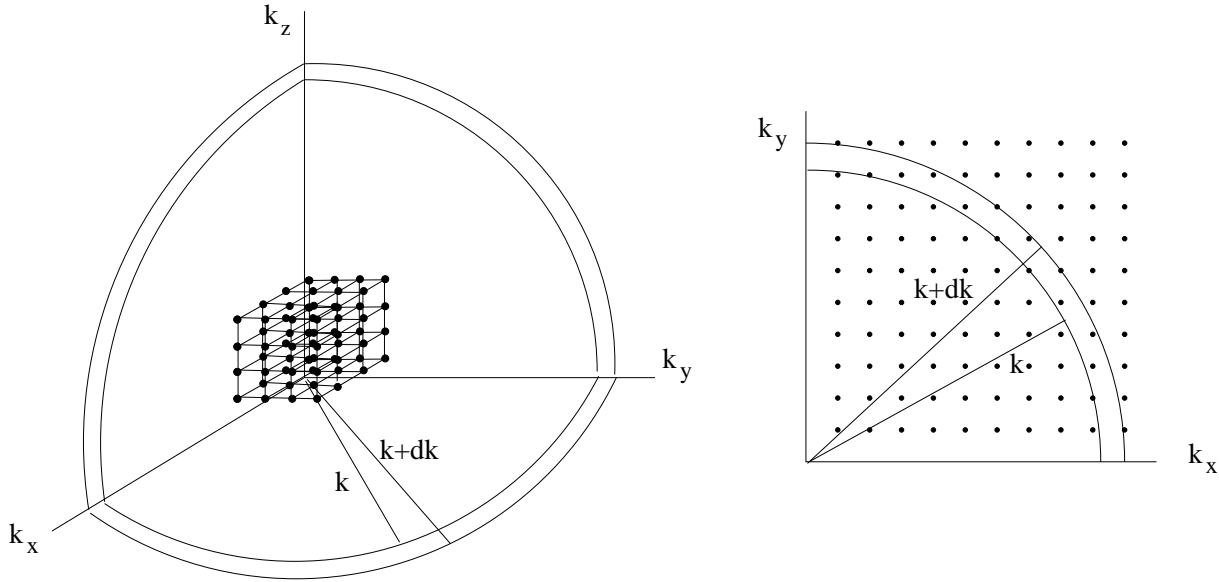
- Mandl 7.1-4, Appendix B
- Bowley and Sánchez 5.9, 7.2
- Kittel and Kroemer 3

4.7.1 The Density of States

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**: $D(k) = V k^2 / 2\pi^2$, so that

$$Z_1 = \int_0^\infty D(k) e^{-\varepsilon(k)\beta} dk$$

We see that $D(k)$ 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

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

with n_x etc positive, the allowed values of \mathbf{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, $(1/8) \times 4\pi k^2 \times dk$, divided by the volume of k -space per state, π^3/V , giving

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

4.8 The Equipartition Theorem

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

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 $\frac{1}{2}k_B T$ to the average energy and $\frac{1}{2}k_B$ to the heat capacity. The oscillator has quadratic kinetic and potential terms:

$$E_{\text{vib}} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2 x^2 \quad 2 \text{ d.o.f, } E \rightarrow k_B T.$$

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):

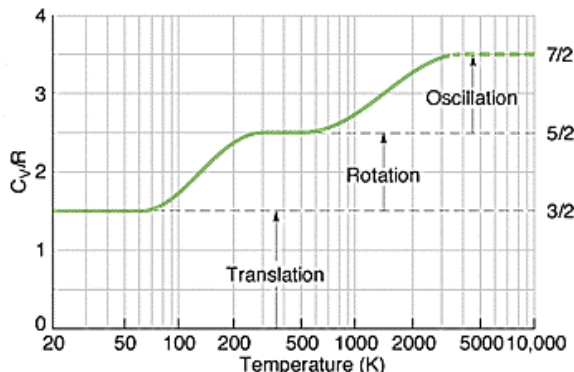
$$E_{\text{rot}} = \frac{1}{2}\mathcal{I}\omega_1^2 + \frac{1}{2}\mathcal{I}\omega_2^2 \quad 2 \text{ d.o.f, } E \rightarrow k_B T.$$

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

$$E_{\text{tr}} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\dot{y}^2 + \frac{1}{2}m\dot{z}^2 \quad 3 \text{ d.o.f, } E \rightarrow \frac{3}{2}k_B T.$$

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 $c\sqrt{p_x^2 + p_y^2 + p_z^2}$ ($= \hbar ck$), not by the quadratic $(p_x^2 + p_y^2 + p_z^2)/2m$, and the average kinetic energy is $3k_B T$, not $\frac{3}{2}k_B T$.

References

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

4.8.1 The heat capacity of a crystal

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

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

At low temperature ($\beta \rightarrow \infty$) 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.

4.9 The ideal gas

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

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.

[Remember](#) the one-particle translational partition function, at any attainable temperature, is

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

From this we can obtain the average energy per particle, $\frac{3}{2}k_B T$, and since the particles are non-interacting, the energy of N particles in a box is just $\frac{3}{2}Nk_B T$. This could be obtained from the expression we [previously](#) used for the N -particle partition function, $Z_N = Z_1^N$, which is justified more generally [here](#).

But if we follow this through and calculate the Helmholtz free energy and the entropy, we find that the results do not make sense: specifically, if one has double the number of particles, in double the volume, the entropy and the Helmholtz free energy, like the energy, should double. These are [extensive](#) variables. But if we go ahead and calculate based on $Z_N = Z_1^N$, we do not get extensive results, but terms like $V \ln N$.

However we shouldn't have expected $Z_N = Z_1^N$ to work, because the [derivation](#) was based on the idea that every one of the N particles was distinguishable. But at a completely fundamental level, every molecule is *exactly* the same as every other molecule of the same substance.

The exact form of Z_N in this case has no compact form. But there is an approximation which becomes exact in the limit of low number densities $n \equiv N/V$: specifically $n \ll n_Q$ where $n_Q \equiv (mk_B T / 2\pi\hbar^2)^{3/2}$ is the “[quantum concentration](#)” and is a measure of the number of energy levels available. It is also proportional to the inverse of cube of the thermal de Broglie wavelength (the wavelength of a particle of energy of order $k_B T$). The significance of this limit is that it is very unlikely that any two atoms are in the same energy level. This is called the **classical limit**.

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

More details of how this works [here](#).

Now, using Stirling's approximation $\ln(N!) \approx N \ln N - N$, we find

$$\begin{aligned}\langle F \rangle &= -k_B T \ln Z_N = -Nk_B T (\ln Z_1 - \ln N + 1) \\ &= -Nk_B T \left[\ln \left(\frac{V}{N} \right) + \ln \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} + 1 \right] \\ &= Nk_B T \left[\ln \left(\frac{n}{n_Q} \right) - 1 \right].\end{aligned}$$

Also

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

and

$$\begin{aligned}S &= - \left(\frac{\partial F}{\partial T} \right)_{V,N} \\ &= -Nk_B \left[\ln \left(\frac{n}{n_Q} \right) - 1 \right] + Nk_B T \frac{dn_Q}{dT} \\ &= Nk_B \left[\ln \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right] \quad \text{The Sackur-Tetrode Equation}\end{aligned}$$

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

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

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 vapourisation, we can numerically calculate the integral

$$\int_{T_0}^T \frac{dQ}{T} = S(T) - S(T_0) \approx S(T)$$

Good agreement is found. An example with numerical details can be found on pages 5&6 [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

$$Z_N = \frac{(Z_1^{\text{tr}})^N (Z_1^{\text{rot}})^N (Z_1^{\text{vib}})^N}{N!} = Z_N^{\text{tr}} (Z_1^{\text{rot}})^N (Z_1^{\text{vib}})^N$$

$$F = F_{\text{tr}} + F_{\text{rot}} + F_{\text{vib}}$$

and the energy and entropy also add.

References

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

4.9.1 Factorisation of partition functions

In lectures, we repeatedly use $Z_N = (Z_1)^N$ for independent distinguishable particles, and we also used $Z_1 = Z_1^{\text{tr}} Z_1^{\text{rot}} Z_1^{\text{vib}}$ 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.

Many-particle system with two single-particle energy levels

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

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

The partition function for two distinguishable particles is

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

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 $0 \leq n \leq N$, and there are $N!/n!(N - n)!$ separate microstate of this energy. So

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

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 the next section.

Many independent subsystems, general case

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

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

Then the full partition function is

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

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):

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

More compactly,

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

4.9.2 The N particle partition function for indistinguishable particles.

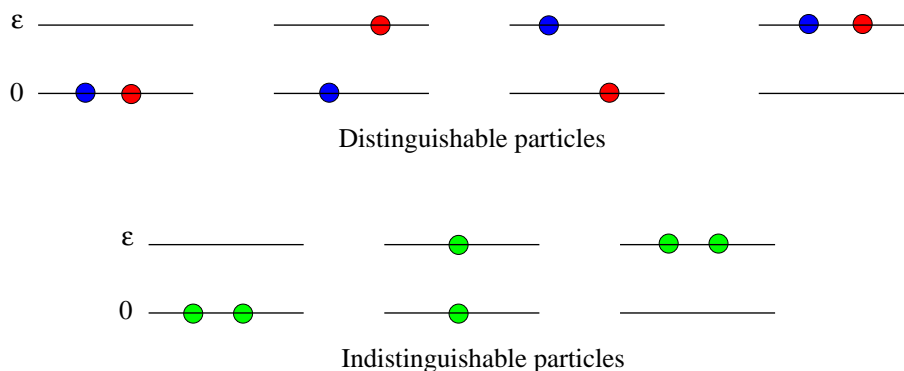
Before reading this section, you should read over the [derivation](#) of $Z_N = (Z_1)^N$ which held for the paramagnet, where all N particles were distinguishable (by their position in the lattice).

Consider first 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

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

If the particles are *indistinguishable*, however, there are only three states, as in the lower picture, and the partition function is

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



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 $k_B T$) 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

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

In the ideal gas, we can calculate the number of levels below, say, $2k_B T$, from $\int_0^{k_{\max}} D(k) dk$ with $\hbar^2 k_{\max}^2 / 2m = 2k_B T$, giving $2.1 n_Q V$. So we see that n_Q is a measure of the number of states available, and we can use the approximation $Z_N = (Z_1)^N / N!$ provided $n_Q V \gg N$ (or $n_Q \gg n$). This is the **classical limit**.

It is worth noting 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 $T \rightarrow 0$, $n_Q \rightarrow 0$ and $S \rightarrow -\infty$. But we know that $S \rightarrow 0$ as $T \rightarrow 0$, 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, $n \approx 3 \times 10^{25} \text{ m}^{-3}$. We have $n_Q \approx n$ for $T \approx 10^{-2} \text{ K}$, so real gases are essentially always classical.

Note too that $n_Q \approx 1/\lambda^3$, where λ is the wavelength of a particle with energy $\frac{3}{2} k_B T$. This implies that the classical limit holds if the particle separation is large compared with their wavelength—a reasonable-sounding statement! (See the first tutorial sheet of last semester, PC210 qu. 1(b-d)).

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 ($n \approx 10^{29} \text{ m}^{-3}$), but at room temperature $n_Q \approx 10^{27} \text{ m}^{-3}$. So the quantum nature of the electron (specifically the fact that it is a fermion) becomes all important.

4.10 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.

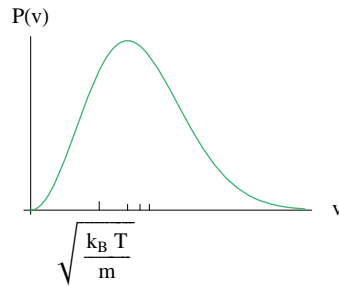
The speed v of a particle is related to the wavenumber k by $mv = \hbar k$. We already know the probability of a particle having k in the range $k \rightarrow k + dk$, and so we can immediately write down the corresponding probability of the speed being in the range $v \rightarrow dv$:

$$P(k \rightarrow k + dk) = \frac{D(k) e^{-\varepsilon(k)\beta}}{Z_1} dk \quad \text{where } \varepsilon(k) = \hbar^2 k^2 / 2m$$

$$P(v \rightarrow v + dv) = \frac{V}{2\pi^2} \frac{e^{-\varepsilon(v)\beta}}{Z_1} \left(\frac{m}{\hbar}\right)^3 v^2 dv \quad \text{where } \varepsilon(v) = mv^2/2$$

$$\Rightarrow P(v) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

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



We can find the most probable speed (from $dP(v)/dv = 0$), as well as the mean speed and the rms speed:

$$v_p = \sqrt{\frac{2k_B T}{m}} \approx 1.41 \sqrt{\frac{k_B T}{m}}$$

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \approx 1.60 \sqrt{\frac{k_B T}{m}}$$

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} \approx 1.73 \sqrt{\frac{k_B T}{m}}$$

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.

References

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

Chapter 5

Systems with variable particle number

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.

5.1 The Gibbs Distribution

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

Now we consider systems which are in contact with a heat bath at temperature T and also in with a particle reservoir at chemical potential μ . The temperature is a measure of the decrease in entropy of the reservoir from giving up heat to the system ([see here](#)); the chemical potential is a measure of the energy decrease (and entropy increase) of the reservoir from giving up particles to the system

We want to find the probability that our system will be in a certain microstate i with an energy ε_i and particle number N_i .

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,

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

gives

$$p_i = \frac{e^{(\mu N_i - \varepsilon_i)/k_B T}}{\mathcal{Z}}$$

with

$$\mathcal{Z} = \sum_j e^{(\mu N_j - \varepsilon_j)/k_B T}$$

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](#)):

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

The quantity $-k_B T \ln \mathcal{Z}$ 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

$$d\Phi_G = -SdT - PdV - Nd\mu$$

and hence

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

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.

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

See [here](#) for more details about Φ_G .

References

- Mandl 11.1
- Bowley and Sánchez 69.7-9
- Kittel and Kroemer 5

5.1.1 The grand potential

The grand potential is

$$\Phi_G \equiv E - TS - \mu N \quad \text{so} \quad d\Phi_G = -SdT - PdV - Nd\mu$$

So $\Phi_G = \Phi_G(T, V, \mu)$. Note that two of the variables T and μ are intensive, so Φ_G , being extensive, must be simply proportional to V , the only extensive one: $\Phi_G = V\phi_G(T, \mu)$. But

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

This also follows from the fact that μ is just the Gibbs free energy per particle (see [here](#)), so $\mu N = G = E - TS + PV$ and hence $PV = -(E - TS - \mu N) = -\Phi_G$.

The fact that Φ_G is so simple doesn't lessen its formal utility in statistical mechanics.

5.2 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:

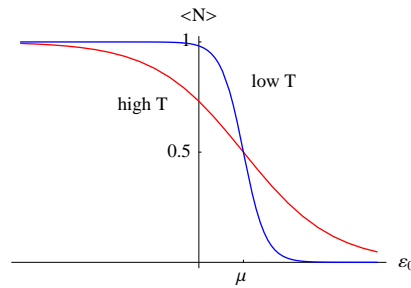
$$\mathcal{Z} = e^0 + e^{(\mu - \varepsilon_0)\beta} = 1 + e^{(\mu - \varepsilon_0)\beta}$$

Then

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

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

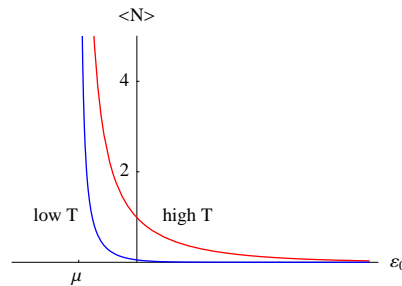


This is less realistic, but we imagine a site which can have any number of molecules occupying it, with energy ε_0 per molecule. There are then infinitely many terms in the grand partition function which form a [geometric series](#):

$$\mathcal{Z} = e^0 + e^{(\mu-\varepsilon_0)\beta} + e^{2(\mu-\varepsilon_0)\beta} + \dots = \frac{1}{1 - e^{(\mu-\varepsilon_0)\beta}}$$

$$\langle N \rangle = \frac{1}{e^{(\varepsilon_0-\mu)\beta} - 1}$$

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.

5.3 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.

Bosons are particles with integer spin:

spin 0: ^1H and ^4He in ground state, pion, Higgs boson

spin 1: ^1H and ^4He 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 $\frac{1}{2}$: ^3He in ground state, proton, neutron, quark, electron, neutrino

spin $\frac{3}{2}$: ^5He in ground state, Δ baryons (excitations of the proton and neutron)

Note that a particle is either a fermion or boson. Excitations will change the spin only by an integer amount. The basic building blocks of atoms are all fermions; 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.

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.

There is no exclusion property for bosons, which 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 ^4He and superconductors.

References

- Mandl 9.2
- Bowley and Sánchez 10.2

5.4 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).

Bose and Fermi gases are the subject of an entire third year course PC3151. This is just a very brief taster.

When we derived the properties of the ideal gas [previously](#), 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. 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

$$\mathcal{Z} = \mathcal{Z}_1 \mathcal{Z}_2 \mathcal{Z}_3 \dots = \prod_r \mathcal{Z}_r$$

where r labels the energy level, not the particle. 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.

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

$$\mathcal{Z}_r = 1 + e^{(\mu - \varepsilon_r)\beta} \quad \langle N_r \rangle = \frac{1}{e^{(\varepsilon_r - \mu)\beta} + 1}$$

and for bosons, which don’t:

$$\mathcal{Z}_r = \frac{1}{1 - e^{(\mu - \varepsilon_r)\beta}} \quad \langle N_r \rangle = \frac{1}{e^{(\varepsilon_r - \mu)\beta} - 1}.$$

(see here.)

For a gas the sum over discrete energy levels is replaced by an integral over the wavenumber k , weighted by the [density of states](#):

$$\langle N \rangle = \int_0^\infty D(k)N(k)dk \qquad \langle E \rangle = \int_0^\infty D(k)\varepsilon(k)N(k)dk$$

where $\varepsilon(k) = \hbar^2 k^2 / 2m$ and

$$N(k) = \frac{1}{e^{(\varepsilon(k)-\mu)\beta} \pm 1} \quad \text{for } \begin{cases} \text{fermions} \\ \text{bosons} \end{cases}$$

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 usually will be) greater than 0.

References

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

5.5 The classical approximation again

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

The last time we calculated the properties of an ideal gas, we regarded the particle number as fixed, but the energy as variable (the temperature being fixed.) 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 isolated gas with fixed energy.

This raises the question of whether we couldn't obtain the same results regarding the particle number as variable also, fixing instead the chemical potential. The answer is that we can of course, as the following shows.

From the previous sections on the [Gibbs distribution](#) and the [ideal gas of bosons or fermions](#), we have

$$\begin{aligned} \Phi_G &\equiv -k_B T \ln \mathcal{Z} \\ &= -k_B T \sum_r \ln \mathcal{Z}_r && \text{using } \mathcal{Z} = \prod_r \mathcal{Z}_r \\ &= \mp k_B T \sum_r \ln (1 \pm e^{(\mu - \varepsilon_r)\beta}) \end{aligned}$$

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

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

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, $Z_1(T) = V n_Q(T)$

From Φ_G we can find the average particle number:

$$N = - \left(\frac{\partial \Phi_G}{\partial \mu} \right)_{T,V} = e^{\mu\beta} Z_1$$

and solving for μ we get

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

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.

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

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

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

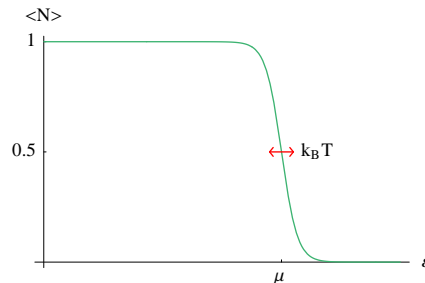
References

- Mandl 11.4
- Bowley and Sánchez 10.2-3

5.6 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.

We have already seen that for electrons in metal, the number of states with energies of order $k_B T$ is much less than 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 $k_B T$ will need to be filled. The occupancy is given by $N(\varepsilon) = 1/(e^{(\varepsilon-\mu)\beta} + 1)$ which is plotted below:



Only levels within a few $k_B T$ of μ have occupancies which are different from 0 or 1. But what is μ ? Normal metals exist in isolated chunks, and are not in contact with “electron reservoirs”. The answer is that we *choose* it so that the metal contains the right number of electrons: $\langle N \rangle = \int_0^\infty D(k) N(k) dk \equiv N$. For copper at room temperature, $\mu \approx 7$ eV, whereas $k_B T \approx 1/40$ eV

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 $\frac{3}{2}k_B T$ predicted by equipartition. 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.

References

- Mandl
- Bowley and Sánchez 10.4.2

5.7 Black-body radiation

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

There are interesting properties of gases of bosonic atoms, but they are beyond the scope of this course. However black-body of cavity radiation can be considered as a gas of photons. The walls of the cavity act as a heat bath; however as photons don't exist in the walls (only energy does) the chemical potential is zero: $\mu = (\partial S_{\text{walls}}/\partial N)_E = 0$. The density of states for the photon gas is just twice the usual density of states (to allow for the two polarisation states) and the energy of a photon with wavenumber k is $\varepsilon(k) = \hbar\omega = \hbar ck$. The total energy in the cavity is

$$\begin{aligned}\langle E \rangle &= \int_0^\infty \frac{2D(k)\varepsilon(k)dk}{e^{\varepsilon(k)\beta} - 1} \\ &= \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3 d\omega}{e^{\hbar\omega\beta} - 1} \\ &= \frac{\pi^2 k_B^4}{15\hbar^3 c^3} VT^4 = \frac{4\sigma}{c} VT^4.\end{aligned}$$

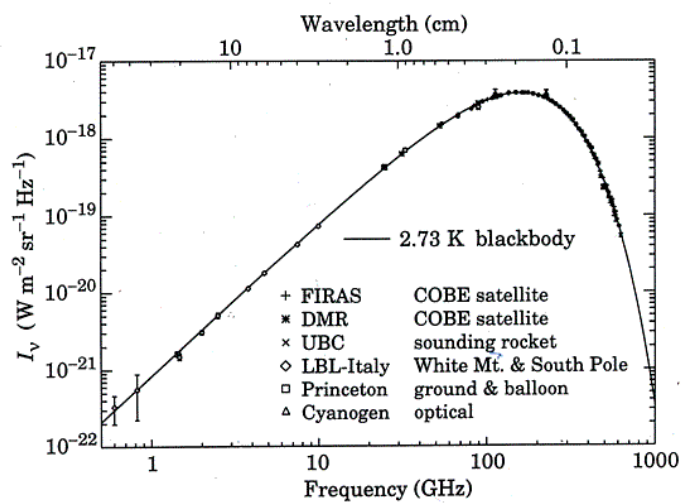
This gives the Planck distribution of energy over the frequency range as well as the derivation of the Stefan-Boltzmann constant σ in terms of fundamental constants.

(The factor of $4/c$ comes from the connection between the cavity energy and the emissivity of a perfect black body, which is given by the formula for effusion from a small hole $dN/dt = -(v/4)An$.)

Below is a plot of the cosmic microwave background at a range of frequencies, obtained from a variety of experiments, compared with the Planck distribution for $T = 2.7$ K (©Douglas Scott of the University of British Columbia). The agreement is excellent.

References

- Mandl 10.4
- Bowley and Sánchez 8.5



Glossary

- **Adiabatic** Of processes: occurring without heat transfer. Of walls: insulating. Reversible adiabatic processes are **isentropic**.
- **Equation of State** A relationship between the state variables of the system. Simple systems in equilibrium are fully specified by two properties such as temperature and volume; all the other functions of state are functions of these. For an ideal gas, the equation of state is $PV = nRT$; for an ideal paramagnet it is $m = cB/\mu_0T$ where c is a constant.
- **Equilibrium** A system is in equilibrium when its macroscopic properties (temperature, pressure) are uniform and not changing with time.
- **Extensive** Some thermodynamic functions of state are extensive: if the intensive variables (T , P , B) are kept constant, the extensive variables are proportional to the amount of substance present. Energy, volume, entropy, total magnetisation, enthalpy, Gibbs and Helmholtz free energies and heat capacities are all extensive. Extensive properties expressed per unit mass or per mole are then intensive, and are called **specific**: eg. specific heat capacity. All functions of state are either extensive or intensive.
- **Function of state** A property of a system which only depends of the current state of the system and not on its history. Examples are temperature, pressure, volume, internal energy, entropy, magnetisation for a paramagnet (but not for a ferromagnet). Also called a **state variable** or a **macroscopic variable**.
- **Heat Reservoir** Surroundings at a certain temperature which are large enough to absorb heat from, or donate heat to, the system without appreciable change of temperature. Also **heat bath**
- **Intensive** An intensive functions of state does not vary with the amount of the substance present. Examples are temperature, pressure, tension and external magnetic field. All functions of state are either extensive or intensive.
- **Isentropic** At constant entropy.
- **Isobaric** At constant pressure.
- **Isochoric** At constant volume.
- **Isothermal** At constant temperature.
- **Macroscopic** Pertaining to aspects of a system which can be measured classically, such as temperature, pressure etc; containing very large numbers of atoms.

- **Macrostate** The current disposition of the system defined in terms of macroscopic variables. Also (in classical thermal physics) **state**.
- **Microscopic** Pertaining to the underlying quantum state of a system
- **Microstate** The state of the system defined in terms of the current behaviour of all the constituent atoms. NOT “the state of a very small system”! Also **quantum state**.
- **Reversible** A reversible process is one which would change direction with an infinitesimal change in external conditions. For a process to be reversible it must be frictionless and quasistatic so that no energy is dissipated and the system is always only infinitesimally removed from equilibrium. Because a reversible process passes through a series of quasi-equilibrium states it can be represented as a solid line on a plot of one state variable against another. More details [here](#).
- **Surroundings** That part of an experimental set up, including the ambient air, which exchanges heat with, or does work on, the system.
- **System** That part of an experimental system in which we are primarily interested.
- **Universe** A deliberately grandiose term for the entire experimental set-up, comprising the system and the surroundings. Usually encountered in the phrase “the entropy change of the universe” which of course cannot be negative, though that of the system or surroundings alone may be. It should not be confused with the cosmological universe.

Ideal Gas: Recap

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

$$PV = nRT \quad \text{or} \quad PV = Nk_B T$$

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), $R = 8.314 \text{ JK}^{-1}$ and $k_B = R/N_A = 1.381 \times 10^{-23} \text{ JK}^{-1}$ 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,

$$E = E(T) \quad \text{and} \quad dE = C_V dT \\ \Rightarrow E = C_V T \quad \text{if } C_V \text{ is constant.}$$

In general the heat capacity may change with temperature; however at STP it is usually adequate to consider it as constant and equal to $\frac{1}{2}n_f R$ 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:

$$C_P - C_V = nR.$$

During reversible adiabatic compression or expansion of an ideal gas the pressure and volume change together in such a way that

$$PV^\gamma = \text{constant} \quad \text{where} \quad \gamma \equiv \frac{C_P}{C_V}$$

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

$$TV^{\gamma-1} = \text{constant} \quad \text{and} \quad TP^{\frac{1}{\gamma}-1} = \text{constant}.$$

Note that $\gamma - 1 = nR/C_V$.

There are two “less ideal” gases sometimes considered. One is a gas of hard spheres, where we no longer neglect the size of the molecules, but still neglect other interactions. Most of the ideal gas results still hold, but with V replaced by $V - nb$, where b is the “excluded volume”, the minimum volume taken up by a mole of the molecules. For instance, the equation of state is $P(V - nb) = nRT$.

The other is the **van der Waals** gas, which also allows for the “van der Waals” interaction between neutral molecules which arise when a fluctuating dipole moment in one molecule induces a dipole in another molecule, and the two attract with a force which falls off as $1/r^6$, with r the separation. This attraction *reduces* the pressure at a given temperature and volume, by an amount which is proportional to $1/V^2$ (or $1/d^6$, where d is the average separation). The equation of state for a van der Waals gas is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT.$$