

Thermal Physics

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These are my notes for the *thermal physics* course from the University of Edinburgh as part of the third year of the theoretical physics degree. When I took this course in the 2020/21 academic year it was taught by Professor Graeme Ackland¹ and Professor Alexander Morozov². These notes are based on the lectures delivered as part of this course, the notes provided as part of this course, and the book ‘Finn’s thermal physics’³. The content within is correct to the best of my knowledge but if you find a mistake or just disagree with something or think it could be improved please let me know.

These notes were produced using L^AT_EX⁴. Graphs were plotted using Matplotlib⁵, NumPy⁶, and SciPy⁷. Diagrams were drawn with tikz⁸.

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³Rex, A. *Finn’s Thermal Physics*, third edition (CRC Press, Boca Raton, 2017)

⁴<https://www.latex-project.org/>

⁵<https://matplotlib.org/>

⁶<https://numpy.org/>

⁷<https://scipy.org/scipylib/>

⁸<https://www.ctan.org/pkg/pgf>

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Acronyms

CFC	chlorofluorocarbon.
CPT	charge parity time.
NPL	national physical laboratory.
PDF	probability density function.

Part I

Thermodynamics

1 The Basics of Thermodynamics

1.1 What is Thermodynamics

The word thermodynamics comes from the Greek θερμός (thermòs), meaning heat, and δύναμις (dunamis), meaning motive force. Thermodynamics is perhaps best described as the study of moving heat. Of particular interest is how to convert heat into motion and vice versa.

One of the most important ideas that we can take away from thermodynamics is a sense of time and causality. In classical mechanics everything is based off of Newton's second law,

$$F = m \frac{d^2x}{dt^2}.$$

If we replace t with $-t$, this is a time transformation all that happens is that the coefficient, m , changes to $-m$:

$$F = -m \frac{d^2x}{dt^2}.$$

This is simply a statement that all process in classical mechanics are reversible. In electromagnetism everything can be built up from Maxwell's equations. Two of these are

$$\nabla \times \mathbf{E} = -\partial_t \mathbf{B},$$

and

$$\nabla \times \mathbf{H} = \mathbf{J} + \partial_t \mathbf{D}.$$

If we replace t with $-t$ in the first of these we get

$$\nabla \times \mathbf{E} = \partial_t \mathbf{B},$$

all that happens is the cross product is negated. This is equivalent to changing from a right handed to left handed system, this is a parity transformation. If we replace t with $-t$ in the second equation and change from a right to left handed system we get

$$\nabla \times \mathbf{H} = -\mathbf{J} + \partial_t \mathbf{D}.$$

This is equivalent to setting all charges, q , equal to $-q$. This is a charge transformation. In quantum mechanics everything is based upon the Schrödinger equation:

$$\frac{1}{2m} \nabla^2 \psi + V\psi = i\partial_t \psi$$

if we replace t with $-t$ we get

$$\frac{1}{2m} \nabla^2 \psi + V\psi = -i\partial_t \psi$$

however both i and $-i$ have the important property of squaring to -1 . This means that this time transformation is the same as choosing to take the negative square root instead of the positive.

The important thing about all of these transformations is that if we reverse time ($t \rightarrow -t$), parity (right \rightarrow left), charge ($q \rightarrow -q$), as well as which square root we take none of the physics changes. This is called charge parity time (CPT) symmetry and is the only symmetry of C, P, and T that exists. CP, CT, and PT symmetry are all violated by some processes in nature but CPT symmetry isn't. This means that all of physics is time reversible if we just reverse a few other things at the same time. This is not true for thermodynamics. The second law of thermodynamics states that entropy will always increase. This means we cannot reverse time. This gives us a way to define cause and effect.

1.2 Equilibrium

An **equilibrium state** is one in which all bulk physical properties do not change with time and are uniform throughout the system. Uniformity only happens if the system is in the same phase throughout. If there is a phase boundary then the system can be split into two or more homogeneous portions, one for each phase. Within each of these portions the properties are uniform, this is what **homogeneous** means.

Isolated systems have equilibrium states that they settle into. Equilibrium states have uniform macroscopic properties, such as pressure, temperature, density, and magnetisation. Surrounding systems need not be in equilibrium with each other.

1.3 System

The **system** is the sample of interest. The system interacts with its surroundings. The system and its surroundings are separated by some kind of boundary wall. The type of boundary wall defines what is held constant, for example

1. if the boundary wall is a moving piston then volume is not held constant. A system where volume *is* held constant is called **isovolumetric**.
2. if the wall is well insulated the amount of heat energy is held constant. A system where the amount of heat energy is held constant is called **adiabatic**.
3. A system that is not insulated will have temperature held constant. A system where temperature is held constant is called **isothermic**.

In a thermodynamic process the way in which system variables change depends on the surroundings.

1.4 State Functions/Variables

Thermodynamics is about macroscopic properties. We care about the temperature, not the speed of individual particles. We care about the volume, density, or mass, not the number of particles. The various properties that can be quantified without disturbing the system are called **state functions** or **state properties**. For example, the internal energy, volume, pressure, and temperature are state functions. Properties whose absolute (as opposed to relative) values are easily measured are called **state variables**. For example, the volume, pressure, and temperature are state variables but the internal energy is not. Relations between state functions are called the **equations of state** of the material. For example for an ideal gas one equation of state is the ideal gas law:

$$PV = nRT.$$

1.5 Zeroth Law of Thermodynamics

We define two systems to be in thermal contact if it is possible for heat to move from one to the other. We define two systems to be in thermal equilibrium if they could be put in thermal equilibrium without any net heat flow between them. The zeroth law of thermodynamics is an experimental law. It states:

Zeroth Law: If two systems are in thermal equilibrium with another system then they are in thermal equilibrium with each other.

This can be extended to any number of systems. The relation, \sim , defined by $A \sim B$ if and only if A is in thermal equilibrium with B is an equivalence relation and the zeroth law is a statement of the transitivity of \sim ⁹.

1.6 Temperature

If systems are in thermal equilibrium with each other they must have some property with a common value. We will call this property the thermodynamic temperature, T_0 , where the 0 denotes that this value is derived from the zeroth law. Note that this is not a numerical system. All we can say given two

⁹See proofs and problem solving course for a definition of an equivalence relation.

systems is that they are either in thermal equilibrium or they aren't and if they aren't then we define the hotter one to be the one that is losing heat energy.

From the ideal gas equation we have

$$T_{IG} = \frac{PV}{nR}$$

which gives us another definition of temperature. This time T_{IG} is a numeric scale. This scale relates to macroscopic properties.

We can also define a third temperature system based off of the kinetic properties of particles:

$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}k_B T_K$$

T_K is again a numerical scale which now relates to the microscopic property of average kinetic energy.

The amazing thing is that it turns out that all three temperature systems, T_0 , T_{IG} and T_K , actually are all equivalent so can be viewed as one temperature system, T , which relates to the zeroth law, the macroscopic properties and the microscopic properties of the system.

The base point for temperature was changed recently. We used to use absolute zero and the triple point of water to define two points on the scale and then filled in around that. We still use absolute zero, we just use a different upper point. It is based off the speed of sound in a gas which is given by

$$c_0 = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_S} = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\frac{\gamma N_A k_B T}{M}}. \quad (1.1)$$

In July 2013 the national physical laboratory (NPL) measured

$$k_B = 1.380\,651\,56(98) \times 10^{-23} \text{ J K}^{-1}.$$

The speed of sound in argon was also measured using a copper sphere whose diameter was known to 11.7 nm, which is approximately 500 atoms in a row. The accurate measure of these values allowed for equation 1.1 to be used to specify a particular temperature more accurately than the triple point of water could. For this reason this is now taken as part of the definition of our temperature scale.

2 Reversibility

2.1 Processes

In Thermodynamics a process is the change of a state variable with time. If a process is reversible then every (infinitesimal) step is reversible for both the system and the surroundings. This involves moving in between equilibrium states. A reversible process is quasi-static, meaning that if the external driving force is removed then the process will halt as it is in an equilibrium state.

An irreversible process is the opposite of a reversible process. It involves moving away from equilibrium states. This means that the state variables are not necessarily the same everywhere during an irreversible process. This means that even something as simple as

$$\int_{P_1}^{P_2} dP$$

can be undefined if P is not the same throughout the system.

In general reversible processes involve a slow process such as a slow compression that allows the system to relax to equilibrium between each infinitesimal step. The equivalent irreversible process would be pushing the piston in quickly. This causes turbulence which is a dissipative process and causes energy to be lost to the surroundings as heat, which is hard to recapture.

When drawing on an indicator diagram, such as a (P, V) diagram, if a process is reversible it can be represented as a continuous line. If it is irreversible this may not be possible. Instead we draw a series of circles representing the range of values that the state variables take at any one time.

It is possible to move between two states by a reversible or irreversible process. The final state of the system will be the same regardless of reversibility. However the state of the surroundings will be different for the different processes.

Example 2.1. Consider a piston of area A being pushed in a distance, dx , by a force, F . The force required is given by $F = PA$ which is simply the definition of pressure, P . The volume change is $dV = A dx$. The work done is $dW = F dx = PA dx = P dV$. For this reason we define work in thermodynamics as $dW = (-)P dV$. If we now wish to find the work done for a finite volume change from V_1 to V_2 we simply integrate:

$$W = \int_{W_1}^{W_2} dW = \int_{V_1}^{V_2} P dV.$$

The total work depends exactly on what the process is. If P is a constant then this integral is trivially $P(V_2 - V_1)$. If we assume an ideal gas then the integral depends on whether we take T as a constant or try to quantify how it changes.

Example 2.2. Consider an ideal gas that expands reversibly from a state, (P_1, V_1, T_1) , to a state, (P_2, V_2, T_2) . Again the work done is

$$W = \int_{V_1}^{V_2} P dV.$$

Consider figure 2.1. The path marked C is an isothermal process. This makes it easy to define the

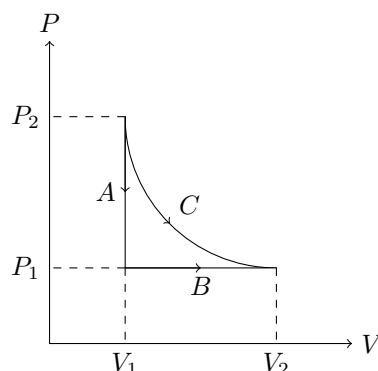


Figure 2.1: Two possible processes for a reversible expansion.

pressure using the ideal gas law with $T = T_1 = T_2$:

$$P = \frac{nRT}{V}.$$

Thus the work done becomes

$$\begin{aligned} W &= \int_{V_1}^{V_2} P dV \\ &= nRT \int_{V_1}^{V_2} \frac{dV}{V} \\ &= nRT \ln \left(\frac{V_2}{V_1} \right). \end{aligned}$$

If instead we consider the non-isothermal process along path A then B we end up at the same point. This time we have to do two integrals. The first is along A and the second along B . Thus the work is

$$\begin{aligned} W &= \int_A P dV + \int_B P dV \\ &= \int_{V_1}^{V_1} P dV + \int_{V_1}^{V_2} P dV \end{aligned}$$

$$\begin{aligned}
&= 0 + P \int_{V_1}^{V_2} dV \\
&= P(V_2 - V_1).
\end{aligned}$$

Here we have used the fact that an integral over $[V_1, V_1]$ is zero so we don't need to know the pressure. We then used the fact that the process that takes us along B is isobaric (constant pressure) so we can factor the pressure out of the integral.

We see that we get two different results for the work done depending on the process, even for a reversible process like this one. In fact we could do an infinite amount of work by just cycling along path A then B and then backwards along C .

2.2 Sign Convention

In physics and chemistry we are usually interested in changes of the system. In engineering the interest is usually in changes of the surroundings. For this reason there is a difference in sign conventions used to define work. It could be $\pm P dV$. We choose¹⁰

$$dW = -P dV.$$

The logic behind this is that if $dV < 0$, i.e. the system is compressed, then the work done is positive. We expect the work done to compress a gas to be positive so this is the correct sign choice for us. The important thing is to think about the sign that you expect *before* attempting a problem.

2.3 Dissipative Processes

For an irreversible process we can't specify the work done by the state variables as these aren't well defined. We can measure the work done on/by the surroundings and use conservation of energy to say what this means for work done on/by the system.

An example of a dissipative process is stirring. The system heats up but $P dV = 0$ as the volume doesn't change. This means this can't possibly be the correct form of the work done. So this process must be dissipating energy in some way. If you stir in the opposite direction, i.e. perform the reverse process, it isn't possible to un-mix or extract energy. We see that stirring is not a reversible process.

Dissipative processes are always irreversible, however not all irreversible processes are dissipative.

2.4 The Maths of Thermodynamics

In thermodynamics we often ask the questions

- How does changing one state variable affect another – this points us towards differential calculus as a solution.
- How does constraining one variable while changing a second affect a third variable – this points us to partial derivatives.

2.4.1 Exact Differentials

Consider a single valued state function, φ , of the variables x and y . If we change x by dx and y by dy the change in φ is given by

$$d\varphi = \left(\frac{\partial \varphi}{\partial x} \right)_y dx + \left(\frac{\partial \varphi}{\partial y} \right)_x dy.$$

The same can be done for a function of more variables. The finite change in φ is given by

$$\Delta\varphi = \varphi(x_2, y_2) - \varphi(x_1, y_1) = \int_{(x_1, y_1)}^{(x_2, y_2)} d\varphi.$$

So we see that $\Delta\varphi$ is uniquely determined by its evaluation at the two points (x_1, y_1) , and x_2, y_2 . The integral is path independent. State variables in thermodynamics have path independent integrals.

¹⁰We will explain the bar through the d in a couple of sections

For example if a process takes a system from the state (T_1, P_1) to (T_2, P_2) then we can find another state variable by integrating along any path between these two points. So we may as well choose one that makes the integral as easy as possible.

We can calculate the change of a state variable due to an irreversible process by calculating the change of that state variable due to an equivalent reversible process. This is only true for the system. We can't do this for the surroundings as the state of the surroundings changes depending on if we follow a reversible or irreversible process but by definition the system is in the same state at the beginning and end of the process.

All state variables, f , of the variables x_i have the property that

$$\frac{\partial^2 f}{\partial x_i \partial x_j} = \frac{\partial^2 f}{\partial x_j \partial x_i}$$

where all the variables that aren't explicitly included are held constant. This means that f is a well behaved, differentiable, function. State variables are almost always well behaved, the one exception is at a phase transition, for example the volume can change discontinuously upon boiling.

If we have two independent variables and f depends on both of them then the variables that we hold constant are important. For the following derivatives describe isothermal and isobaric compression and are in general not equal:

$$\left. \frac{\partial f}{\partial V} \right|_T \neq \left. \frac{\partial f}{\partial V} \right|_P.$$

2.4.2 Inexact Differentials

If something is not a state variable then it does not have an exact differential. We denote the inexact differential with a bar, such as $\bar{d}W$, to remind us of this. The integral over this variable is dependent on the path, this is what it means to be inexact. We consider the argument from before in reverse. Suppose that the integral over $\bar{d}\varphi$ is path dependent. Therefore we cannot simply write

$$\int \bar{d}\varphi = \varphi(\mathbf{x}_2) - \varphi(\mathbf{x}_1)$$

where \mathbf{x}_1 and \mathbf{x}_2 are simply vectors of state variables. The fact that we can't write this means that φ is not a state function.

Work is not a state function. We can show this by showing that the order of partial derivatives matters. The inexact differential for work is $\bar{d}W = -P dV$. The question that we ask is if there exists a function, W , of variables P and T such that

$$\bar{d}W = \left(\frac{\partial W}{\partial P} \right)_V dP + \left(\frac{\partial W}{\partial V} \right)_P dV?$$

We still require that $\bar{d}W = -P dV$ so from this we must have

$$\left(\frac{\partial W}{\partial P} \right)_V = 0, \quad \text{and} \quad \left(\frac{\partial W}{\partial V} \right)_P = -P.$$

Calculating second derivatives we get

$$\begin{aligned} \frac{\partial}{\partial V} \left(\left(\frac{\partial W}{\partial P} \right)_V \right)_P &= \frac{\partial}{\partial V} (0)_P = 0 \\ \frac{\partial}{\partial P} \left(\left(\frac{\partial W}{\partial V} \right)_P \right)_V &= \frac{\partial}{\partial P} (-P)_V = -1 \end{aligned}$$

Since $0 \neq -1$ we have that

$$\frac{\partial^2 W}{\partial P \partial V} \neq \frac{\partial^2 W}{\partial V \partial P}.$$

Hence W is not a state function. The order of derivatives is important and the integral is path dependent. Remember that in example 2.2 the path that we chose affected the work done.

To summarise

- State variables in thermodynamics have path independent integrals.
- Reversible processes in thermodynamics have path dependent integrals.
- Irreversible processes in thermodynamics have no well defined integrals.

Example 2.3. The state of a fluid undergoes an infinitesimal, reversible, change from (P, T) to $(P + dP, T + dT)$. What is the change in volume? Start by writing the volume as a function of relevant state variables, $V = V(P, T)$. The change in volume is then

$$\begin{aligned} dV &= \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \\ &= -\frac{K}{V} dP + \beta V dT \end{aligned}$$

where K is the bulk modulus, which characterises isothermic compression, and β is the thermal expansivity, which characterises isobaric compression. They are defined by

$$K = -V \left(\frac{\partial P}{\partial V}\right)_T, \quad \text{and} \quad \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P.$$

V is a state function so we can choose any path. We choose a reversible, two-stage path; an isotherm from P to $P + \Delta P$ and then an isobar from T to $T + \Delta T$. The total volume change is then given by the integral over these two paths. For the first path $dT = 0$ as it is an isotherm. Thus we have

$$\int \frac{1}{V} dV = - \int \frac{1}{K} dP \implies \ln \left(\frac{V_2}{V_1}\right) = -\frac{\Delta P}{K}.$$

For the second path $dP = 0$ as it is an isobar. Thus we have

$$\int \frac{1}{V} dV = - \int \beta dT \implies \ln \left(\frac{V + \Delta V}{V_1}\right) = \beta \Delta T.$$

After some rearranging we get

$$V + \Delta V = V e^{-\Delta P/K} e^{\beta \Delta T}.$$

Notice that V_1 disappears as this was just an intermediate value that we introduced to define a path. We would have also gotten the same result if we started with the isobar and then the isotherm. If we had considered an irreversible process the answer would have been the same even though the integral is not defined for that process.

3 Heat

Take some ice, put it in some water. Does all the ice melt? What temperature does the water end up? The process for answering these questions is to consider the following process:

- The water cools to 0°C . This releases $Q_l = m_l c_l \Delta T_l$ where the symbols have their usual meanings and l denotes that these are for the liquid water.
- The ice warms to 0°C . This takes $Q_s = m_s c_s \Delta T_s$ where g denotes that these are for the solid water.
- The ice melts. This takes $E = m_s l_{\text{vap}}$.
- Depending on the sign of the left over energy one of two things will happen next:
 - If the left over energy is positive it is used to heat the water by $\Delta T = (Q_l + Q_s + E)/[(m_l + m_s)c_l]$.
 - If the left over energy is negative some of the ice freezes again. We end up with a mass of ice given by $m = -(Q_l + Q_s + E)/l_{\text{vap}}$.

This successfully answers the question even though this process is not the same as what actually happens. For example if the energy left at the end is negative then not all the ice will melt in the first place. The fact that we can do this means there must be a state function related to the energies that we are computing with. We will see later in this section what that is.

3.1 What is Heat?

James Joule used falling weights to turn paddles in water and measured a temperature rise. He found that the same amount of mechanical work, mgh , always produced the same rise in temperature. He also found that he could use electrical work to produce this same temperature rise. This showed that heat could be produced by work alone. Previously heat had been thought of as an element that each material had a finite amount of and could be released by processes such as burning. However by putting in an arbitrary amount of mechanical or electrical work Joule showed that an arbitrary amount of heat could be produced and so it necessarily had to come from the work.

As a result of being able to use different forms of work to produce the same change in a system we must have that when a thermally isolated system is brought from one equilibrium state to another the work necessary is independent of the process used. This observation requires that there is a state function related to heat, we call it the internal energy, U . It was found that

$$\Delta U = U_2 - U_1 = W_{\text{adiabatic}}$$

where the last term is the work done in a process that allows no heat to flow out of the system. Essentially this means that the work done in a process, if it can't go anywhere else, goes to increase the internal energy of the system. Notice that this equation doesn't give us a way to define a point where $U = 0$, we can only define internal energy relative to the internal energy in some other state.

This equation is a restricted form of the first law of thermodynamics. In this form it applies only to a thermally insulated system and cannot be applied to the whole universe.

If we now allow heat transfer then we find that

$$\Delta U = U_2 - U_1 = W + Q$$

where W is the work done on the system and Q is the heat going into the system (in other contexts this may have a different sign for heat leaving the system). Heat is the exchange of internal energy between the system and the surroundings that cannot be identified as work.

What counts as heat therefore depends on how we define our system. If we have a room with a heater and a box of gas then there are two logical ways to define the system. The first is as just the box of gas. In this case the energy given out by the heater which is absorbed by the gas is counted as heat. If instead we define the whole room as the system then the heater is no longer a source of heat for the system it is a source of electrical work and, assuming the walls are well insulated, $Q = 0$. In a way heat and work are just two sides of the same coin.

3.2 First Law of Thermodynamics

First Law: The change in internal energy, dU , of a system is given by the sum of the work done on the system, dW , and the heat transferred to the system, dQ :

$$dU = dW + dQ.$$

Note that $\int dW$ and $\int dQ$ are both path dependent but their sum, $\int dU$ is not. Often we are interested in the work done mechanically on a compressible fluid¹¹, we know in this case that the work done is $dW = -P dV$ and so the first law of thermodynamics is

$$dU = -P dV + dQ.$$

Typical forms of work that we need to account for are electrical, magnetic, or gravitational. Typical forms of internal energy are kinetic energy and potential energy, which in turn includes chemical, nuclear, and gravitational energy, as well as mass energy due to relativity. Fortunately since internal energy is always defined relatively we only need to account for sources of internal energy that change. For example if we are compressing a gas we don't need to account for chemical, nuclear, gravitational, or mass energy unless we start compressing the gas so much that it starts reacting with itself or undergoing nuclear fusion, and this is unlikely.

Another important feature is that due to the path independence of $\int dU$ the first law of thermodynamics has time reversal symmetry.

¹¹Remember that fluid encompasses both liquids and gasses.

3.3 Heat Capacity

The heat capacity, C , of a material that is heated by ΔQ , and has a temperature increase of ΔT . is defined to be

$$C = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T} = \frac{dQ}{dT}.$$

This definition is useful for theoretical work but for practical calculations we define two more useful quantities: the specific heat capacity, $c = C/m$, where m is the mass of the system, the specific heat capacity then gives the energy needed to heat 1 kg of the substance by 1 K. We also define the molar heat capacity, $c = C/n$ ¹², where n is the number of moles of the substance, the molar heat capacity then gives the energy needed to heat 1 mol of the substance by 1 K.

As normal with thermodynamics a definition that doesn't specify what is constant isn't very useful. If we hold volume constant then the heat capacity at constant volume is C_V . We start with a rearrange form of the first law of thermodynamics:

$$dQ_V = dU_V + P dV_V.$$

Importantly we are holding V constant so $dV_V = 0$ which means $dQ_V = dU_V$.

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

If instead we hold the pressure constant then $dQ_P = dU_P + P dV_P$. We define the enthalpy, H , to be $H = U + PV$. In differential form this becomes

$$dH = d(U + PV) = dU + P dV + V dP.$$

Holding P constant gives us

$$dH_P = dU_P + P dV_P$$

since $dP_P = 0$ when pressure is held constant. Further we know that $dU_P = -P dV_P + dQ_P$ so substituting this into the enthalpy gives us

$$dH_P = -P dV_P + dQ_P + P dV_P = dQ_P.$$

Finally this allows us to calculate the heat capacity at constant pressure:

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

Notice that heat capacity is a state variable, unlike heat.

3.3.1 Relation Between C_V and C_P

From the first law of thermodynamics

$$dQ_P = dU_P + P dV_P$$

dividing through by dT and taking a limiting process while holding pressure constant gives us the heat capacity at constant pressure again:

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (3.1)$$

Now let $U = U(T, V)$, then a small change in these state variables produces the following change in U :

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (3.2)$$

¹²Yes, that is the same symbol as specific heat capacity, thermodynamics has too many letters, and an inexplicable refusal to use Greek letters like any other self respecting field of physics would.

Dividing through by dT and taking a limiting process while holding pressure constant gives us

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P.$$

We can identify the first term on the right hand side as C_V :

$$\left(\frac{\partial U}{\partial T}\right)_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P.$$

We can now substitute this into equation 3.1 to get

$$C_P = C_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P.$$

Subtracting C_V and factorising we get

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P.$$

This is the best we can do in general, however if we consider an ideal gas then the internal energy is dependent only on the pressure. This means that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

for an ideal gas. This means

$$C_P - C_V = P \left(\frac{\partial V}{\partial T}\right)_P.$$

From the ideal gas law we have

$$V = \frac{nRT}{P} \implies \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}.$$

Thus

$$C_P - C_V = P \frac{nR}{P} = nR. \quad (3.3)$$

Now looking at equation 3.2 for an ideal gas we see that final term is zero and so

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_V dT. \quad (3.4)$$

We will use this in future calculations.

3.3.2 Reversible, Isothermal, Ideal Gas Expansion

For an isothermal expansion $\Delta T = 0$. The ideal gas law gives us

$$P = \frac{nRT}{V} \propto \frac{1}{V}$$

this means that on a (P, V) -indicator diagram we expect isotherms, that is lines of constant temperature, to be hyperbola. Since we are considering a reversible process we know that the work done on the system is the negative of the work done on the surroundings. We can fairly easily find the work done on the surroundings:

$$W = \int dW = \int P dV_T = nRT \int \frac{dV}{V} = nRT \ln \left(\frac{V_2}{V_1} \right).$$

3.3.3 Reversible, Adiabatic, Ideal Gas Expansion

For an adiabatic expansion $\Delta Q = 0$ so $\Delta U = \Delta W$. Similarly $dQ = 0$ so applying equation 3.4 and the first law of thermodynamics gives us

$$0 = dQ = dU + P dV = C_V dT + P dV.$$

Using the ideal gas law to replace P , and then the relationship that we derived for an ideal gas in equation 3.3, that $C_P - C_V = nR$, we get

$$0 = C_V dT + \frac{nRT}{V} dV = C_V dT + (C_P - C_V) \frac{T}{V} dV.$$

Rearranging gives us

$$-\frac{C_V}{T} dT = (C_P - C_V) \frac{1}{V} dV.$$

Integrating gives us

$$-C_V \int \frac{dT}{T} = (C_P - C_V) \int \frac{dV}{V}$$

which we evaluate as

$$-C_V \ln T = (C_P - C_V) \ln V + \ln A$$

where $\ln A$ is a constant of integration. Applying log laws gives us

$$\ln T^{-C_V} = \ln (AV^{C_P - C_V}).$$

Exponentiating gives

$$T^{-C_V} = AV^{C_P - C_V}.$$

Multiplying through by T^{C_V} gives

$$1 = AT^{C_V} V^{C_P - C_V}.$$

Raising everything to the power of $1/C_V$ gives

$$1 = A^{1/C_V} T V^{C_P - 1}.$$

Multiplying through by A^{-1/C_V} and defining $\gamma = C_P/C_V$ we get

$$A^{-1/C_V} = T V^{\gamma - 1}.$$

Since A and C_V are constants we conclude that $TV^{\gamma - 1}$ is a constant. From the ideal gas law we know that

$$T = \frac{PV}{nR}$$

and so the constant $TV^{\gamma - 1}$ in this form is

$$TV^{\gamma - 1} = \frac{PV}{nR} V^{\gamma - 1} = \frac{P}{nR} V^\gamma.$$

Since n and R are constants and the left hand side is a constant we must have that PV^γ is constant. If instead we write the volume using the ideal gas law:

$$V = \frac{nRT}{P}$$

then the constant PV^γ becomes

$$PV^\gamma = P \left(\frac{nRT}{P} \right)^\gamma = P^{1-\gamma} (nR)^\gamma T^\gamma.$$

Since γ is a constant and so are n and R we have that $P^{1-\gamma} T^\gamma$ is a constant, or as it is more usually written by raising everything to the power of $1/\gamma$: $TP^{(1-\gamma)/\gamma}$ is constant.

3.4 Irreversible Free Expansion and the Joule Coefficient

A rigid, adiabatic, container is partitioned into two equal volumes, one which is a vacuum and the other which contains a gas. The system we consider is this all of the gas in the container. The irreversible process in question is the breaking of the partition. No work is done on the system and there is no heat transfer so the internal energy is constant and $dU = 0$. We can write the temperature as a state function, $T = T(U, V)$. A small change in these state variables causes the following change in the temperature:

$$\begin{aligned} dT &= \left(\frac{\partial T}{\partial V} \right)_U dV + \left(\frac{\partial T}{\partial U} \right)_V dU \\ &= \left(\frac{\partial T}{\partial V} \right)_U dV \\ &= \mu_J dV. \end{aligned}$$

This is the definition of μ_J , called the **Joule coefficient**, it characterises temperature change due to a volume change. For an ideal gas U depends only on the temperature. This means that for U to be constant we must have the state start and end at the same temperature. Therefore $\mu_J = 0$.

4 Heat Engines

A heat engine turns heat into work. They do so by a cyclic process. Every cycle the system returns to an initial equilibrium. However the surroundings do not return to the same state and work is done. All of the steps of the cycle are quasi-static meaning reversible. During each step the values of the state variables change and the system exchanges heat and mechanical energy with its surroundings.

4.1 Carnot Engine

The most efficient heat engine is the Carnot engine. It follows that Carnot cycle:

- Isothermal expansion
- Adiabatic expansion
- Isothermal compression
- Adiabatic compression

During the isothermal expansion heat, Q_1 , is absorbed, then during the isothermal compression heat, Q_2 , is given out. The stages drawn on a (P, V) -indicator diagram form a closed loop. The work done is the area enclosed by this loop. The surroundings of the Carnot engine consist of two constant temperature heat reservoirs. In each step of the process there is a piston moving. The heat exchange can only occur along the isotherms since by definition there is no heat exchange along an adiabat. Every cycle the work done is $W = Q_1 - Q_2$. Reversing the process requires an input of work and heat is moved from one reservoir to the other. This is the process by which a refrigerator works.

4.2 General Heat Engine

The internal energy is constant. Therefore by the first law of thermodynamics we know that

$$0 = \Delta Q + \Delta W = Q_1 - Q_2 - W \implies W = Q_1 - Q_2.$$

Notice that we define work done by the engine to be positive as opposed to the more normal work done on the system being positive. This is because an engine doing positive work makes more sense so we switch convention when talking about engines. The **efficiency** of any process is the ratio of useful energy out to total energy in. For the heat engine the efficiency is

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}.$$

Perhaps a more useful quantity in practice is the power. Power is simply the useful energy per second which is the work done per cycle times the number of cycles per second. There is a balance to be had here, we could have very efficient but slow cycles if we were going for peak efficiency but if we want peak power then there will be some optimal speed which may not be at peak efficiency.

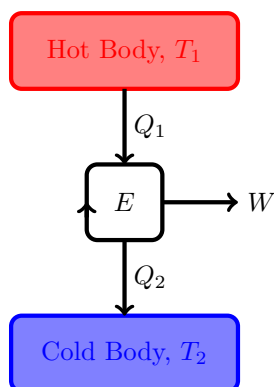


Figure 4.1: The basic workings of a heat engine

4.3 Second Law of Thermodynamics

The second law of thermodynamics defines certain processes to be impossible even if they still follow the first law. There are two equivalent statements:

Clausius statement:

Second Law: It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body.

Kelvin–Planck statement:

Second Law: It is impossible to construct a device that, operating in a cycle, produces no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work.

Clausius' statement forbids heat to flow from cold to hot even if the total energy is conserved. What this means is that for a refrigerator it is impossible to have $Q_1 = Q_2$ without also putting in work. The Kelvin–Planck statement forbids heat to be converted into work with 100 % efficiency. What this means is that for an engine it is impossible to have $Q_2 = 0$.

Broadly the first law forbids processes where the energy out is different than the energy in and the second law says that the energy out will always have a contribution that we cannot use for driving another process.

We can draw heat engines for the forbidden processes described in both of these statements. This is done in figure 4.2 We can fairly easily show that the two statements of the second law are equivalent. First

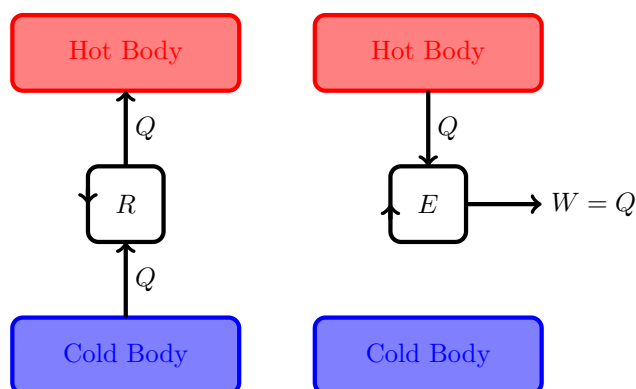


Figure 4.2: Heat engines forbidden by the second law

suppose that Kelvin–Planck is false but Clausius still stands. We use a Kelvin–Planck violating engine, E , to drive a refrigerator, R . If both E and R have the same hot and cold bodies then E extracts heat, Q_1 , from the hot body and converts it entirely to work, W , which is then used to run R . R extracts heat Q_2 from the cold body and delivers $Q_2 + W = Q_2 + Q_1$ to the hot body since the total energy into R must be equal to the total energy out by the first law. If we then treat the system including both E

and R as one composite refrigerator, $E + R$, then $E + R$ extracts Q_2 from the hot body and delivers Q_2 to the cold body. This violates Clausius so our assumption that Kelvin–Planck doesn't hold must be wrong. Hence Clausius implies Kelvin–Planck. We can see the systems in question in figure 4.3. We can

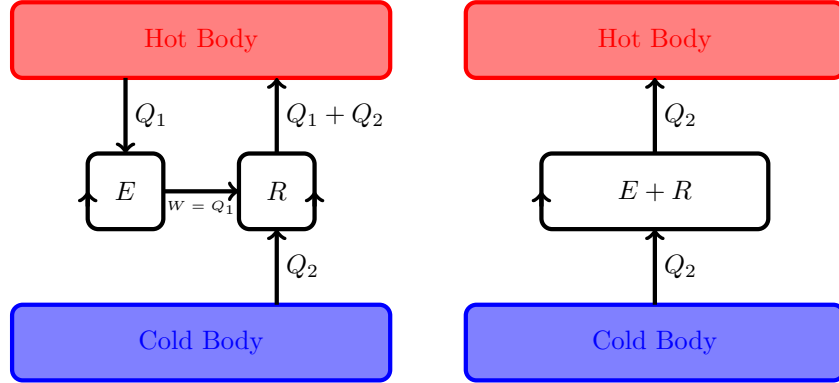


Figure 4.3: A composite system which violates Clausius.

show that Kelvin–Planck implies Clausius in a similar way.

4.4 Carnot Engine Again

Carnot's theorem is

Carnot's Theorem: No engine operating between two reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

This is fairly easy to prove. Suppose that we had an engine E' with efficiency η' and a Carnot engine C with efficiency η_C . Now suppose that E' violates Carnot's theorem so that when operating between the same reservoirs $\eta' > \eta_C$. We can tune both engines such that they do equal amounts of work, $W = W'$. The efficiency of E' is

$$\eta' = \frac{W'}{Q'_1} = \frac{W}{Q'_1}.$$

The efficiency of C is

$$\eta_C = \frac{W}{Q_1}.$$

For $\eta' > \eta_C$ to hold we require that

$$Q_1 > Q'_1.$$

Since a Carnot engine only exchanges heat along isotherms it is reversible with the same efficiency. Thus if we instead use C as a refrigerator it will have efficiency η_C still. If we use E' to drive C as a refrigerator then the process acts to move heat $Q_1 - Q'_1$ from cold to hot without any external work being done. Since $Q_1 > Q'_1$ this quantity is positive so this composite system, $E' + C$, violates Clausius' statement of the second law. This means that our assumption that E' is more efficient than a Carnot engine is false.

It is however possible that $\eta' = \eta_C$, this would mean that there is no heat flow in the composite system. We conclude that

$$\eta' \leq \eta_C.$$

Suppose that we have two Carnot engines, C_a and C_b with efficiencies η_{C_a} and η_{C_b} respectively. Since we can use the first to drive the second or vice versa then applying the above proof to these two engines we have $\eta_{C_a} \leq \eta_{C_b}$ and $\eta_{C_b} \leq \eta_{C_a}$ so $\eta_{C_a} = \eta_{C_b}$. This means that all Carnot engines operating between the same two reservoirs have exactly the same efficiency independent of the way that the two engines operate, as long as they follow the Carnot cycle. This is a direct Corollary of Carnot's theorem.

Another corollary of Carnot's theorem is a temperature scale. Since the efficiency of any reversible heat engine operating between the same two reservoirs is equal the efficiency,

$$\eta_R = 1 - \frac{Q_2}{Q_1},$$

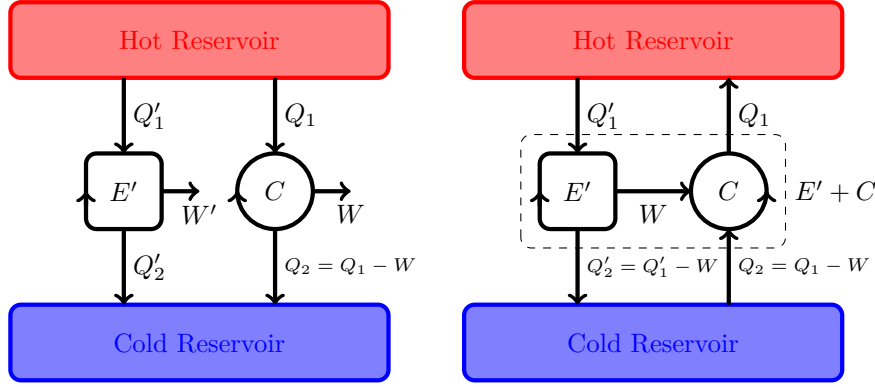


Figure 4.4: Systems used to prove Carnot's theorem

can only depend on the temperatures of the reservoirs as these are the only variables that need to be the same for all engines. Therefore there must be a universal function, $f: \mathbb{R}^2 \rightarrow \mathbb{R}$ such that

$$\frac{Q_2}{Q_1} = f(T_1, T_2)$$

for all heat engines. Here T_1 and T_2 are the temperatures of the hot and cold reservoirs respectively. We can consider the form of f by considering another composite system where one engine runs on the waste heat of another. This system is shown in figure 4.5. Tuning the engines so that $Q_2 = Q_2'$ we can consider this composite system as a single engine since no net heat enters the reservoir at T_3 so we don't need a reservoir at all. We know that

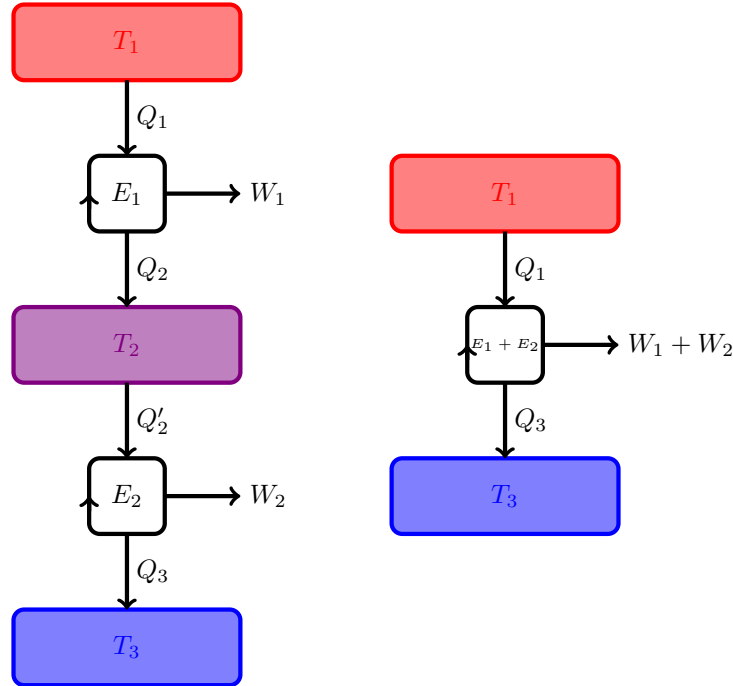


Figure 4.5: One heat engine running on the waste heat of another.

$$f(T_1, T_2) = \frac{Q_2}{Q_1}, \quad \text{and} \quad f(T_2, T_3) = \frac{Q_3}{Q_2}.$$

For the composite engine

$$f(T_1, T_3) = \frac{Q_3}{Q_1}.$$

From this we see that

$$f(T_1, T_3) = \frac{Q_3}{Q_1} = \frac{Q_3}{Q_2} \frac{Q_2}{Q_1} = f(T_2, T_3) f(T_1, T_2).$$

From this we see that f must factorise as

$$f(T_1, T_2) = \frac{\vartheta(T_1)}{\vartheta(T_2)},$$

where ϑ is a universal function of temperature for whatever temperature scale we use to measure T . We can then use ϑ as a temperature scale. We will show in a later section that $\vartheta(T) = T_{\text{IG}}$ where T_{IG} is the temperature as defined by the ideal gas law.

5 More Heat Engines

5.1 Thermodynamic Temperature Scale

In the last section we defined a temperature scale, ϑ , based on the efficiency of a Carnot engine. We will show that this temperature scale is the same as the temperature scale, T , that appears in the ideal gas law. To do this we consider the Carnot cycle with an ideal gas as our working substance.

The first stage of the Carnot cycle is isothermal expansion from a volume V_a to V_b . For an ideal gas the internal energy is a function of the temperature, $U = U(T)$. Since this is isothermal expansion T is constant so U must also be constant. The first law then gives us

$$0 = dU = dq - P dV_T \implies dq = P dV_T.$$

Integrating this we get that the heat into the ideal gas, q_{ab} , is

$$q_{ab} = \int_{q_a}^{q_b} dq = \int_{V_a}^{V_b} P dV_T = nRT_1 \int_{V_a}^{V_b} \frac{dV_T}{V} = nRT_1 \ln \left(\frac{V_b}{V_a} \right).$$

This is positive as the process is expansion so $V_b > V_a$ meaning the argument of the logarithm is greater than one.

The third stage in the Carnot cycle is isothermal compression from V_c to V_d . Applying the same logic as for expansion the heat absorbed by the system is

$$q_{cd} = nRT_2 \ln \left(\frac{V_d}{V_c} \right).$$

Since this is compression $V_d < V_c$ so the argument of the logarithm is less than one so q_{cd} is negative.

The other two stages are adiabatic so there is no heat exchange. If we now consider the heat exchange with the sign conventions that we use with engines then we can identify that $q_{ab} = Q_1$ and $-q_{cd} = Q_2$. The ratio of these two heats is

$$\frac{Q_2}{Q_1} = \frac{-nRT_2 \ln(V_d/V_c)}{nRT_1 \ln(V_b/V_a)} = \frac{T_2 \ln(V_c/V_d)}{T_1 \ln(V_b/V_a)}. \quad (5.1)$$

We now look at the adiabatic expansion from V_b to V_c and adiabatic compression from V_d to V_a . Since these processes are adiabatic we know that $TV^{\gamma-1}$ must be constant. Hence

$$T_1 V_b^{\gamma-1} = T_2 V_c^{\gamma-1}, \quad \text{and} \quad T_1 V_a^{\gamma-1} = T_2 V_d^{\gamma-1}.$$

Dividing the first of these by the second we can show that

$$\frac{V_b}{V_c} = \frac{V_c}{V_d}.$$

This means that the values of the logarithms in equation 5.1 are the same so we have

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}.$$

Therefore we can define $\vartheta(T) = T$ and we will have that the ideal gas temperature and the thermodynamic temperature are the same. This allows us to rewrite the efficiency of the Carnot heat engine:

$$\eta_C = 1 - \frac{T_2}{T_1}.$$

5.2 Efficiency of Carnot Engines

There are three ways to use the Carnot cycle, and more generally any heat engine. The first is as a heat engine where heat in from the hotter reservoir is turned into work. The efficiency of this is

$$\eta = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}.$$

For the Carnot cycle this becomes

$$\eta_C = 1 - \frac{T_2}{T_1}.$$

The second way we can use one of these cycles is as a refrigerator. In this case work in is used to remove heat from the cold reservoir. The efficiency of this, sometimes called the coefficient of performance, is

$$\eta^R = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}.$$

For a Carnot cycle this becomes

$$\eta_C^R = \frac{T_2}{T_1 - T_2}.$$

The third way that we can use the cycle is one we haven't discussed yet. We can use the cycle as a heat pump where work is done to add heat to the hot reservoir. This is subtly different from removing heat from the cold reservoir when it comes to efficiency since the goal is different. The efficiency is

$$\eta^{HP} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2}.$$

For a Carnot cycle this becomes

$$\eta_C^{HP} = \frac{T_1}{T_1 - T_2}.$$

One case that is worth considering is when $Q_1 = Q_2$. Here the efficiencies of the refrigerator and heat pump become infinite. This is because the heat flow becomes spontaneous since $Q_1 = Q_2$ means that $T_1 = T_2$.

5.3 Steam Engines

A steam engine makes use of a phase change to create rapid expansion. Work can be extracted from this expansion with either a piston or turbine. It is also often possible to skip the compression stages by simply dumping the steam and adding new water. The steam engine operates at temperatures and pressures where there can be liquid and vapour at the same time.

5.4 Otto Cycle

The Otto cycle is a simplified version of a two stroke petrol engine. The simplification comes by assuming that instead of internal combustion there is an external heat source. The cycle is as follows:

- Reversible adiabatic compression from (P_a, V_1, T_a) to (P_b, V_2, T_b) .
- Isochoric (constant volume) heat exchange from (P_b, V_2, T_b) to (P_c, V_2, T_c) . Heat, Q_1 , is absorbed in this step.
- Reversible adiabatic expansion from (P_c, V_2, T_c) to (P_d, V_1, T_d) . Heat, Q_2 , is extracted from the system
- Isochoric heat exchange from (P_d, V_1, T_d) to (P_a, V_1, T_a) .

Isochoric heat exchange is much faster than isothermal heat exchange meaning that this engine can produce much more power than a Carnot engine.

In the first stage a piston moves in compressing the gas. Since this is adiabatic $dQ = 0$ so the first law gives $dU = dW$. Also

$$T_a V_1^{\gamma-1} = T_b V_2^{\gamma-1}.$$

The work done is

$$\mathrm{d}W = C_V(T_a - T_b).$$

In the second stage heat is added at constant volume. This means $\mathrm{d}W = 0$. The heat therefore is

$$Q_1 = \mathrm{d}U = C_V(T_c - T_b).$$

In the third stage the piston moves out again and we have

$$T_d V_1^{\gamma-1} = T_c V_2^{\gamma-1}$$

and

$$\mathrm{d}W = C_V(T_c - T_d).$$

In the final stage heat is given out and the working substance cools to its original temperature. In reality the working substance is just given out as exhaust and then replaced. The heat given out is

$$Q_2 = C_V(T_d - T_a).$$

The efficiency is

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_d - T_a}{T_c - T_b} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \frac{1}{r_c^{\gamma-1}}$$

where $r_c = V_1/V_2$ is the ratio of the volume of the cylinder with the piston out to the volume of the cylinder with the piston in. That is the compression ratio. Typically $r_c \approx 5$ and $\eta \approx 50\%$. This ignores other inefficiencies that mean that in reality the efficiency is much less than 50%.

A four stroke engine has exhaust and intake stages as well. Note that the efficiency depends on γ which is a property of the gas being used. For a diatomic gas γ is greater than for a monatomic gas. This means that a diatomic gas based Otto cycle is less efficient than for a monatomic gas based Otto cycle. This is because for a diatomic gas some of the heat is used to increase the rotational energy of the molecules which cannot be extracted by a piston. For a monatomic gas this doesn't happen and all of the heat goes to increase the kinetic energy of the gas which we can extract using a piston.

5.5 A Real Engine

We can model a real engine as a Carnot engine with two more heat exchange processes. We include a term, Q_L , that gives the heat lost to surroundings before it can be used for work. We also include Q_F which accounts for heat loss due to friction after work has been produced. This is shown in figure 5.1. The Kelvin-Planck statement of the second law means that $Q_F > 0$ and the Clausius statement of the

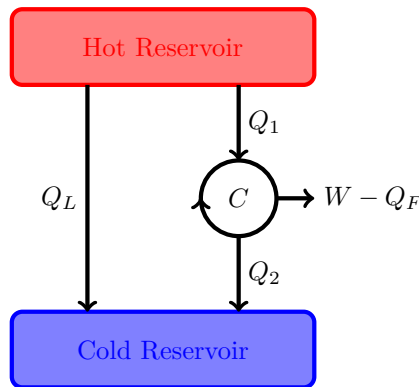


Figure 5.1: A real engine as a Carnot engine with inefficiencies.

second law means that $Q_L > 0$. The efficiency is

$$\eta = \frac{W - Q_F}{Q_1 + Q_L} < \frac{W}{Q_1}$$

so we see that a real engine must always be less efficient than an ideal engine.

6 Entropy

6.1 The Clausius Inequality

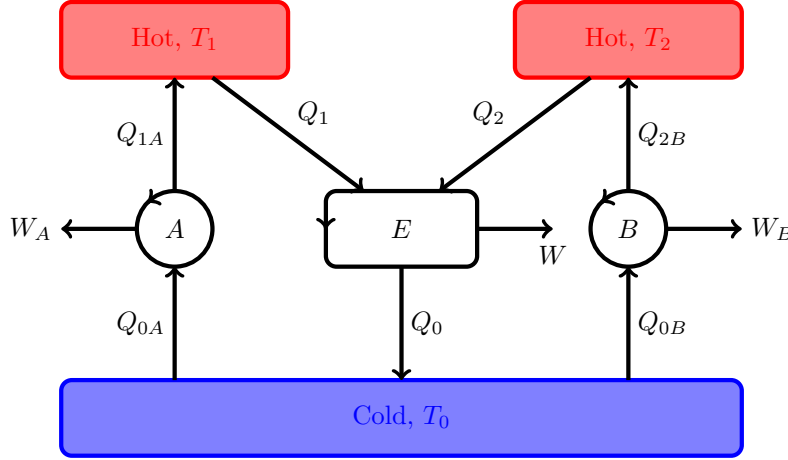


Figure 6.1: The setup for demonstrating Clausius' inequality

Consider the setup in figure 6.1. A and B are Carnot refrigerators and E is an engine. There are two hot heat reservoirs at temperatures T_1 and T_2 and a cold heat reservoir at temperature T_0 . We adjust the engines so that there is no net heat flow to the hot heat reservoirs, that is

$$Q_{1A} = Q_1, \quad \text{and} \quad Q_{2B} = Q_2.$$

The net heat flow out of the cold reservoir is

$$Q_{0A} + Q_{0B} - Q_0.$$

We expect this to be negative (i.e. heat is entering the cold reservoir).

We consider as a system both fridges and the engine. The total work done by the system is

$$W - (W_A + W_B).$$

We adjust the engine so that there is not heat flow into or out of the heat reservoirs. Hence the internal energy is a constant so $Q_T = W_T$ where Q_T is the total heat absorbed by the system and W_T is the total work done by the system (following the engine sign convention). Hence we have

$$Q_{0A} + Q_{0B} - Q_0 = W - (W_A + W_B).$$

This will violate the Kelvin-Planck statement of the second law unless

$$W \leq W_A + W_B, \quad \text{and} \quad Q_{0A} + Q_{0B} - Q_0 \leq 0.$$

Using the efficiency of the Carnot refrigerators we know that

$$\frac{Q_{1A}}{Q_{0A}} = \frac{T_1}{T_0} \implies Q_{0A} = Q_1 \frac{T_0}{T_1},$$

and similarly

$$Q_{0B} = Q_2 \frac{T_0}{T_2}.$$

The heat leaving the cold reservoir is

$$Q_{0A} + Q_{0B} - Q_0 = \left(\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \right) T_0 - Q_0 \leq 0.$$

Hence

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} - \frac{Q_0}{T_0} \leq 0.$$

We now consider heat inputs, q_i , into the working substance of the engine. The engine absorbs $q_1 = Q_1$ and $q_2 = Q_2$ from the hot reservoirs and returns heat Q_0 to the cold reservoir so $q_0 = -Q_0$. The inequality above then becomes

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} + \frac{q_0}{T_0} \leq 0.$$

This generalises to any number of engines and refrigerators.

$$\sum_i \frac{q_i}{T_i} \leq 0.$$

Be careful, T_i are the temperatures of the reservoirs with which heat is exchanged, not the temperatures of the system.

In the limit where each engine absorbs only an infinitesimal amount of heat, $\mathrm{d}q$, from a large number of reservoirs all at temperature T this becomes

$$\int \frac{\mathrm{d}q}{T} \leq 0.$$

This is the **Clausius inequality**. Be careful, T is the temperature of the surroundings, not the system.

6.2 Entropy

If we apply the Clausius inequality to a reversible system something interesting happens. For a reversible process the system and surroundings must be in equilibrium so the temperature of the system, T_{sys} , is the same as the temperature of the surroundings, T_{surr} . Performing the process forward the Clausius inequality must hold so

$$\int \frac{\mathrm{d}q_R}{T} \leq 0.$$

However since this is a reversible process we can also perform it in to opposite direction. If we do this then the heat absorbed in each infinitesimal stage is $-\mathrm{d}q_R$ but T is the same so the Clausius inequality becomes

$$-\int \frac{\mathrm{d}q_R}{T} \leq 0.$$

The only way that both of these can hold is if

$$\int \frac{\mathrm{d}q_R}{T} = 0.$$

Consider a reversible cycle from state i to state f and back to i along path 1 from i to f and path 2 from f to i . We can split the integral at i and f and we have

$$\oint \frac{\mathrm{d}q_R}{T} = \int_{i \text{ path 1}}^f \frac{\mathrm{d}q_R}{T} + \int_{f \text{ path 2}}^i \frac{\mathrm{d}q_R}{T} = 0$$

Hence

$$\int_{i \text{ path 1}}^f \frac{\mathrm{d}q_R}{T} = - \int_{f \text{ path 2}}^i \frac{\mathrm{d}q_R}{T} = \int_{i \text{ path 2}}^f \frac{\mathrm{d}q_R}{T}.$$

This shows that this integral is independent of the path. This means that $\mathrm{d}q_R/T$ is an exact differential even though $\mathrm{d}q_R$ is not. There must, therefore, be a state function, S , such that

$$\Delta S = S_f - S_i = \int_i^f \mathrm{d}S = \int_i^f \frac{\mathrm{d}q_R}{T}.$$

We call this state function entropy. Notice that this equation only defines a change in entropy. It doesn't give us a point where $S = 0$ and it doesn't tell us what physical property entropy is a measure of.

If path 1 were instead irreversible then the Clausius inequality is

$$\oint \frac{\mathrm{d}q}{T} = \int_{i \text{ path 1}}^f \frac{\mathrm{d}q}{T} + \int_{f \text{ path 2}}^i \frac{\mathrm{d}q_R}{T} \leq 0.$$

This implies that

$$\int_i^f \text{path 1} \frac{\dot{d}q}{T} \leq - \int_f^i \text{path 2} \frac{\dot{d}q_R}{T} = \int_i^f \text{path 2} \frac{\dot{d}q_R}{T} = \Delta S.$$

Note that even though this is an irreversible process we can still do the integral as T is the temperature of the surroundings and $\dot{d}q$ is the heat exchanged with the surroundings and these are defined quantities even though the temperature of the system may not be defined. What this means is that the change in entropy for an irreversible process is always less than the change in entropy for an equivalent reversible process, that is

$$\int_i^f \frac{\dot{d}q}{T} \leq \int_i^f dS,$$

with equality if and only if the integral on the left is performed over some reversible process.

Example 6.1. Water at 20 °C is placed in thermal contact with a heat reservoir at 100 °C. The water is heated irreversibly at constant pressure to an equilibrium state at 100 °C. What is the change in entropy of the water and of the surroundings?

We consider the water as the system. The process is irreversible so we work with an alternative, reversible, process. The surroundings in this reversible process are a series of heat reservoirs each at a slightly higher temperature. This heats the water slowly in a way that is reversible. At each intermediate step in this process there is a reversible transfer of heat, $dQ = C_P dT$, from the surroundings to the system. The change in entropy of this intermediate step is then

$$dS = \frac{dQ}{T} = \frac{C_P dT}{T}.$$

The total entropy change is then

$$\Delta S^{\text{sys}} = C_P \int_{T_i}^{T_f} \frac{dT}{T} = C_P \ln \left(\frac{T_f}{T_i} \right) \approx 0.241 C_P.$$

For the change in entropy of the surroundings we again consider an alternative, reversible, process. This time the process is a series of heat reservoirs, each slightly cooler than the last, which represents the heat transferred to the system. The total heat transferred is

$$-C_P(T_f - T_i)$$

and the change in entropy is

$$\Delta S^{\text{surr}} = \frac{C_P(T_f - T_i)}{T_f} \approx -0.21448 C_P.$$

The total entropy change is then

$$\Delta S^{\text{tot}} = \Delta S^{\text{sys}} + \Delta S^{\text{surr}} = 0.02693 C_P > 0.$$

Consider an adiabatic, thermally isolated system. Then T is a constant and $\dot{d}q = 0$. Thus $dS \geq 0$ where equality holds only for a reversible process. This is a statement that entropy never decreases.

We now have four equivalent statements of the second law of thermodynamics:

- Heat can't flow from a cooler reservoir to a hotter reservoir.
- Heat cannot be converted to work with 100 % efficiency.
- Reversible cycles are the most efficient engines possible.
- Entropy cannot decrease.

We can think of heat as the lowest form of energy. All forms of energy tend towards heat as time progresses. This is a statistical phenomenon. There are more ways for energy to be heat, that is the motion of particles, than any other form of energy. Therefore heat is the most likely form of energy.

The second law is the only fundamental equation in physics which violates charge parity time (CPT) symmetry. We use this to define a 'forward' direction in time.

7 The Central Equation of Thermodynamics

If we combine the first law,

$$dU = dQ + dW,$$

and the definition of entropy,

$$dS = \frac{dQ}{T},$$

along with the mechanical work done, $-P dV$, compressing a fluid, we get the **central equation of thermodynamics**:

$$dU = T dS - P dV.$$

This is useful as it involves only state variables. This means that we can integrate it along any path. For an irreversible process we can find an equivalent reversible process along which to integrate. This also gives us $T dS = dU + P dV$ which is an easier way to measure dS than the original definition of dQ/T .

An extensive property of a material is one that depends on how much of the material there is, such as volume or internal energy. Contrastingly an intensive property of a material is one that doesn't depend on how much of the material there is, such as density or temperature. Since the central equation gives us the entropy in terms of the extensive properties U and V the entropy must also be an extensive property.

This equation can be made more general if we consider different kinds of work. For example, if a charge, Z , is moved by an emf \mathcal{E} , then the work done is $\mathcal{E} dZ$. The central equation is then

$$dU = T dS - P dV + \mathcal{E} dZ.$$

If instead we consider a rubber band of length L being stretched by a force, F , then the work done in stretching the rubber band dominates and the central equation becomes

$$dU = T dS + F dL.$$

7.1 Entropy of an Ideal Gas

We showed in equation 3.4 that for an ideal gas $dU = C_V dT$. Using this, and the ideal gas equation, the central equation becomes

$$dS = C_V \frac{dT}{T} + nRT \frac{dV}{V} = C_V \frac{dT}{T} + Nk_B \frac{dV}{V}.$$

If we look at values per mole this becomes

$$ds = c_V \frac{dT}{T} + R \frac{dv}{v}$$

where lowercase symbols have the same meaning as their uppercase counter parts but per mole. Integrating this gives

$$s = c_V \ln T + R \ln v + s_0$$

where s_0 is some constant of integration.

This breaks down as $T \rightarrow 0$ as $s \rightarrow -\infty$. This is more than just the fact that the ideal gas equation makes several assumptions and also that kinetic theory breaks down at low temperatures. Fundamentally the reason this doesn't work is that, as we will see later, entropy is about counting things and for that things need to be discretised.

7.2 Entropy change in Joule Expansion

In free expansion of an ideal gas there is no work done or heat exchanged. Hence $dU = dQ + dW = 0$. This means the internal energy is constant. Since the internal energy of an ideal gas is a function only of its temperature this means that the temperature must be constant and so $dT = 0$. The volume however does change. Therefore there is a change in entropy:

$$ds = c_V \frac{dT}{T} + R \frac{dv}{v} = R \frac{dv}{v}.$$

Integrating this from initial volume v_i to final volume v_f we get

$$\begin{aligned}\Delta s &= s_f - s_i = \int_{s_i}^{s_f} ds = R \int_{v_i}^{v_f} \frac{dv}{v} = R \ln \left(\frac{v_f}{v_i} \right) \\ \implies v_f &= v_i e^{(s_f - s_i)/R}.\end{aligned}$$

Example 7.1. Consider the same setup as example 6.1. Water is heated from 20 °C to 100 °C at a constant pressure in an irreversible way. We have already seen one method for calculating the entropy and here we will discuss two more. Recall that the method that we have seen is to directly calculate

$$\Delta S = \int_i^f \frac{dq_R}{T} = \int_i^f \frac{C_p dT}{T}$$

for some alternative reversible process.

The second method we can use is to integrate the central equation:

$$\Delta S = \int_i^f \frac{dU}{T} + \int_i^f \frac{P}{T} dV.$$

To do this we expand dU and dV in terms of P and T . We choose P and T as P is constant and T is the variable that we are interested in changing. We get

$$\Delta S = \int_i^f \frac{1}{T} \left[\left(\frac{\partial U}{\partial T} \right)_P dT + \left(\frac{\partial U}{\partial P} \right)_T dP \right] + \int_i^f \frac{P}{T} \left[\left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP \right].$$

Since pressure is constant this reduces to

$$\begin{aligned}\Delta S &= \int_i^f \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_P dT + \int_i^f \frac{P}{T} \left(\frac{\partial V}{\partial T} \right)_P dT \\ &= \int_i^f \frac{1}{T} \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT \\ &= \int_i^f \frac{1}{T} \left(\frac{\partial}{\partial T} [U + PV] \right)_P dT \\ &= \int_i^f \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P dT.\end{aligned}$$

Comparing this to the result we got with the first method we see that

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

The third method we can use is to use the enthalpy for a constant pressure process:

$$H = U + PV$$

Differentiating we get

$$dH = dU + P dV + V dP.$$

Substituting for dU with the central equation we get

$$dH = T dS - P dV + P dV + V dP = T dS + V dP.$$

At constant pressure this becomes

$$dH_P = T dS_P.$$

Integrating this gives

$$\int_i^f dS_P = \int_i^f \frac{1}{T} dH_P.$$

Writing $H = H(T, P)$ we see that

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP.$$

At constant pressure this becomes

$$dH_P = C_P dT.$$

Integrating this gives

$$\int_i^f dS_P = \int_i^f \frac{1}{T} dH_P = \int_i^f \frac{C_P}{T} dT,$$

as we found previously.

These three methods are the most common approaches to calculating the entropy in a thermodynamics problem:

1. Try to define a process, or an alternative reversible process if the process in question is irreversible. This is usually the longest way to solve a problem but is mathematically the simplest.
2. Integrate the central equation with the correct work term and with careful consideration of what is held constant and what isn't. This is often relatively quick but mathematically trickier.
3. Use the 'correct' thermodynamic variable. For example at constant pressure the enthalpy often gives useful values. This is why chemists like enthalpy so much. This is fast if we know the 'correct' variable to use but not much use if we don't.

7.3 Entropy Change in the Universe

Heat water from T to $T + \Delta T$. The entropy change of the water and surroundings are

$$\Delta S_{\text{sys}} = C_P \ln \left(\frac{T + \Delta T}{T} \right),$$

and

$$\Delta S_{\text{surr}} = C_P \frac{\Delta T}{T}.$$

These were calculated in example 6.1. If we define $x = \Delta T/T$ then the total entropy change is

$$\Delta S_{\text{tot}} = C_P [x - \ln(1 + x)].$$

This is non-negative for all $x > -1$. We see that for positive T the entropy must increase.

Example 7.2. Consider an emf, \mathcal{E} , driving a current, I , through a resistor, R , in an adiabatic box. The power output is $I^2 R$. No heat or mechanical work is exchanged with the surroundings so the total internal energy change in time Δt is

$$\Delta U = I^2 R \Delta t.$$

Electrical work is dissipated irreversibly as heat,

$$\Delta U = C_V \Delta T,$$

which must all go to heating up the box since it is adiabatic. The change in temperature can be calculated:

$$\Delta T = \frac{I^2 R \Delta t}{C_V}.$$

What is the change in entropy?

Volume is constant so $dV = 0$, therefore the central equation becomes

$$dS = \frac{dU}{T} \implies dS = \frac{C_V dT}{T}.$$

Integrating gives us

$$\Delta S = \int_T^{T+\Delta T} \frac{C_V}{T} dT.$$

Alternatively we could have defined an equivalent reversible heating process and found that

$$\Delta S = \int_T^{T+\Delta T} \frac{dq_R}{T} = \int_T^{T+\Delta T} \frac{C_V dT}{T}.$$

Either way the entropy change is

$$\Delta S = C_V \ln \left(1 + \frac{I^2 R \Delta t}{T C_V} \right).$$

Again as $T \rightarrow 0$ we now have $\Delta S \rightarrow \infty$. So this breaks down when temperatures are near zero.

7.4 Statistical Entropy

This section will be expanded upon in the statistical mechanics part of this course.

The total entropy can be defined as

$$S = k_B \ln \Omega$$

where Ω is the total number of ways it is possible to arrange the system. For example, consider Joule expansion where one box, A , full of gas is allowed to expand freely into a second box, B , which is initially under a vacuum. After this expansion the probability that any one atom is in box A is $1/2$. The probability that all atoms are in box A is $1/2^N$ where $N \sim N_A$ is the number of atoms, clearly this is incredibly unlikely. The probability that 50% of the atoms are in box A is

$$\binom{N}{N/2} \frac{1}{2^N}.$$

In general the probability that r of the atoms are in box A is

$$\binom{N}{r} \frac{1}{2^N}.$$

The maximum value of this comes at $r = N/2$ which means that the state where the atoms are evenly distributed between the two boxes is the most likely. This is also the highest entropy state since it is more likely precisely because there are more arrangements of the system that lead to this arrangement.

The number of possible states with all particles

1. in A is $\Omega(N, V, E)$
2. in A or B is $\Omega(N, 2V, E)$.

If all accessible microstates are equally likely then

$$\frac{\Omega_A}{\Omega_{A+B}} = \frac{\Omega(N, V, E)}{\Omega(N, 2V, E)} = \frac{1}{2^N}.$$

We can justify the form of this definition of entropy heuristically. Suppose that there exists a function, f , such that $f(\Omega) = S$. Entropy, being an extensive property, is additive. That is if a system is formed from two subsystems with entropies S_1 and S_2 then the total entropy is

$$S = S_1 + S_2.$$

Permutations on the other hand are multiplicative. That is if a system is formed from two subsystems which can be arranged in Ω_1 and Ω_2 ways then the total number of arrangements of the whole system is

$$\Omega = \Omega_1 \Omega_2.$$

Hence we must have

$$f(\Omega) = f(\Omega_1 \Omega_2) = f(\Omega_1) + f(\Omega_2) = S_1 + S_2.$$

This holds if $f(\omega) = \ln \omega$. Thus for fixed energy, E , we define

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

One important factor that comes from this is that Ω involves counting things which means that said ‘things’ need to be discretised which leads to quantum mechanics.

8 Thermodynamic Potentials

A mechanical equilibrium is reached when the energy is minimised. A thermodynamic equilibrium is reached when entropy is maximised. We define the free energy as the thermodynamic variable that is minimised to reach a thermodynamic equilibrium. This is useful as the entropy is often difficult to measure and therefore not very useful for practical applications. We have already met two such variables that we can minimise for equilibrium and we will introduce some more. These variables are called **free energies** or **thermodynamic potentials**. Which thermodynamic potential we work with depends on which state variables we are working with. The thermodynamic potentials are themselves state variables and therefore can be written as a function of two other state variables. Typically we choose the two variables that simplify the maths, which often means one variable that is held constant and one variable that we control the change in. The thermodynamic potentials and the natural variables to work in are given in table 8.1. Which potential we choose depends on what the situation is. In chemistry most

Potential	Differential	Natural Units
Internal energy, U	$dU = T dS - P dV$	S, V
Enthalpy, $H = U + PV$	$dH = T dS + V dP$	S, P
Helmholtz free energy ¹³ , $F = U - TS$	$dF = -P dV - S dT$	T, V
Gibbs free energy, $G = H - TS$	$dG = V dP - S dT$	T, P

Table 8.1: The thermodynamic potentials

experiments are open to the atmosphere so P is constant. The temperature is also readily measured and controlled. This means that often the Gibbs free energy, G , is the best potential to use. In physics we often work with S and T as constants, for example, a pendulum swinging. Therefore we work with internal energy, $dU = -dW$, for some appropriate expression of work.

In mechanics we often start with a Hamiltonian, \mathcal{H} , and we assume that \mathcal{H} is the sum of the kinetic and potential energies. This assumes that we have boundary conditions of S and V being constant and therefore we can use $\mathcal{H} = U$. If instead we study air as a sound wave passes then S and P are the variables of interest so we should use $\mathcal{H} = H$. If we study reagents dissolved in water then we have T and V being the variables of interest so we should use $\mathcal{H} = F$. If we study water exposed to the atmosphere then we have T and P being the variables of interest so we should use $\mathcal{H} = G$. In general we look at any boundaries in the system and at what variables are either constant or can change over those boundaries.

8.1 Maxwell Relations

State functions can usually be written as function of two independent variables. Therefore there must be a relationship between the state functions. The equation of state is one such relationship that is material specific. There are also relationships that are general and true due to the mathematical nature of the state variables. In particular we can use the fact that the potentials are state variables and therefore represented by nice functions of their natural variables and partial derivatives commute. This allows us to derive four relations called the Maxwell relations.

We start with

$$dU = T dS - P dV.$$

Taking a derivative with respect to V at constant entropy we have

$$\left(\frac{\partial U}{\partial V}\right)_S = -P.$$

Taking a derivative with respect to S at constant volume we have

$$\frac{\partial^2 U}{\partial S_V \partial V_S} = -\left(\frac{\partial P}{\partial S}\right)_V.$$

¹³sometimes denoted A

Since partial derivatives commute if we compute this in the other direction we must get the same result:
First

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

then

$$\frac{\partial^2 U}{\partial V_S \partial S_V} = \left(\frac{\partial T}{\partial V}\right)_S.$$

So we conclude

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

Next we start with

$$dH = T dS + V dP.$$

$$\begin{aligned} \Rightarrow \left(\frac{\partial H}{\partial S}\right)_P = T &\Rightarrow \frac{\partial^2 H}{\partial P_S \partial S_P} = \left(\frac{\partial T}{\partial P}\right)_S \\ \Rightarrow \left(\frac{\partial H}{\partial P}\right)_S = V &\Rightarrow \frac{\partial^2 H}{\partial S_P \partial P_S} = \left(\frac{\partial V}{\partial S}\right)_P \\ \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P. \end{aligned}$$

Next we start with

$$dF = -P dV - S dT$$

$$\begin{aligned} \Rightarrow \left(\frac{\partial F}{\partial V}\right)_T = -P &\Rightarrow \frac{\partial^2 F}{\partial T_V \partial V_T} = -\left(\frac{\partial P}{\partial T}\right)_V \\ \Rightarrow \left(\frac{\partial F}{\partial T}\right)_V = -S &\Rightarrow \frac{\partial^2 F}{\partial V_T \partial T_V} = -\left(\frac{\partial S}{\partial V}\right)_T \\ \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T. \end{aligned}$$

Finally we start with

$$dG = V dP - S dT$$

$$\begin{aligned} \Rightarrow \left(\frac{\partial G}{\partial P}\right)_T = V &\Rightarrow \frac{\partial^2 G}{\partial T_P \partial P_T} = \left(\frac{\partial V}{\partial T}\right)_P \\ \Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S &\Rightarrow \frac{\partial^2 G}{\partial P_T \partial T_P} = -\left(\frac{\partial S}{\partial P}\right)_T \\ \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P &= -\left(\frac{\partial S}{\partial P}\right)_T. \end{aligned}$$

All four relations are:

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial S \partial V} \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial S \partial P} \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial^2 F}{\partial T \partial V} \\ -\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial T \partial P} \end{aligned}$$

8.2 Remembering the Thermodynamic Potentials and Maxwell Relations

In the Maxwell relations the natural variables of the relevant potential are the ones that appear in the denominator. For a derivative like

$$\left(\frac{\partial x}{\partial y}\right)_z$$

xz has units of energy.

The following mnemonic gives us the potentials and Maxwell's relations:

Good Physicists Have Studied Under Very Fine Teachers.

We use this to remember the potentials and state variables in the order G, P, H, S, U, V, F, T . We then place these anticlockwise around a square as shown in figure 8.1. The natural variables for describing a

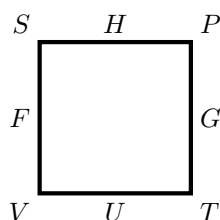


Figure 8.1: Mnemonic for remembering thermodynamic potentials and Maxwell relations.

potential are then the two variables on the same line as it, for example $H = H(S, P)$. This means that we can write

$$dH = \text{sign const } dS + \text{sign const } dP.$$

The constants are given by the diagonal opposite of the state variables that make up the differential:

$$dH = \text{sign } T dS + \text{sign } V dP.$$

Finally we get the sign by drawing an arrow from the constant to the differential. If the arrow is up then the sign is positive, if it is down then the sign is negative, the arrows are shown in figure 8.2:

$$dH = T dS + V dP.$$

We can get the Maxwell relations for two state variables by picking the two variables that aren't

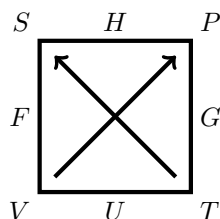


Figure 8.2: Using the mnemonic to find the thermodynamic potentials.

diagonally opposite, for example S and V . We then start with the form

$$\left(\frac{\partial V}{\partial ?}\right)_{\text{const}} = \text{sign} \left(\frac{\partial S}{\partial ?}\right)_{\text{const}}.$$

We draw arrows along the diagonals from the variables of interest, this is shown in figure 8.3. The thing that is held constant is given by the end of the arrow:

$$\left(\frac{\partial V}{\partial ?}\right)_P = \text{sign} \left(\frac{\partial S}{\partial ?}\right)_T.$$

The variable we differentiate with respect to is given by the end of the other arrow:

$$\left(\frac{\partial V}{\partial T}\right)_P = \text{sign} \left(\frac{\partial S}{\partial P}\right)_T.$$

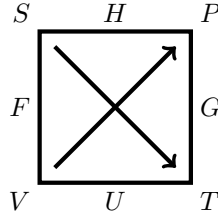


Figure 8.3: Using the mnemonic to find Maxwell's relations

If both arrows are up or both are down then the sign is positive, else the sign is negative:

$$\left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial S}{\partial P}\right)_T.$$

8.3 $T dS$ Equations

Using these relations we can find the entropy in terms of other, more easily measured variables:

$$T dS = c_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dv,$$

$$T dS = c_P dT - T \left(\frac{\partial V}{\partial T}\right)_P dP,$$

and

$$T dS = c_p \left(\frac{\partial T}{\partial V}\right)_P dv + c_V \left(\frac{\partial T}{\partial P}\right)_V dP.$$

These are called the $T dS$ equations.

8.4 Gay–Lussac Law

The Gay–Lussac law, also known as Amonton's law, is that the ratio of pressure and temperature is a constant, known as the Gay–Lussac constant, k_{GL} :

$$k_{GL} = \frac{P}{T}.$$

If we assume an isothermal process then

$$k_{GL} = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T.$$

This constant, k_{GL} , is a property of the material.

8.5 Iso-

Iso-, from the Greek, ἴσος (isos) meaning equal, is a prefix usually used to denote that a quantity is constant for a certain process:

- Isotropic – Equal in all directions,
- Isotopic – Equal element,
- Isothermal – Equal temperature,
- Isobaric – Equal pressure,
- Isochoric/Isovolumetric – Equal volume,
- Isenthalpic – Equal enthalpy,
- Isoenergetic – Equal energy,
- Isentropic – Equal entropy,
- Adiabatic – Equal heat.

8.6 Minimising Thermodynamic Potentials

We started the section by claiming that minimising the relevant thermodynamic potential was the same as maximising the entropy. In this section we will show this for a specific system. Suppose a gas, initially at temperature T and pressure P is placed in thermal contact with a temperature and pressure reservoir at temperature T_0 and pressure P_0 . Also the gas and reservoir are adiabatically separated from the rest of the universe and there is a free (meaning able to move) wall between the system and the reservoir. Initially the system is out of equilibrium. Heat, Q , flows between the system and the reservoir. The change in entropy of the surroundings is

$$\Delta S_0 = -\frac{Q}{T_0}.$$

The change in volume of the surroundings is

$$\Delta V_0 = \Delta V = \frac{W}{P_0}.$$

The second law means

$$\Delta S_{\text{sys}} + \Delta S_0 \geq 0.$$

The first law is

$$Q = \Delta U + P_0 \Delta V.$$

Combining these we have

$$\Delta U + P_0 \Delta V - T_0 \Delta S_0 \leq 0.$$

Since P_0 and T_0 are constant for a pressure and temperature reservoir this can be written as

$$\Delta(U + PV - TS) \leq 0. \implies \Delta(H - TS) \leq 0 \implies \Delta G \leq 0.$$

We made no assumptions about which way the system had to move to reach equilibrium so we see that any step that the system makes towards equilibrium will decrease G therefore the system is in equilibrium when G is minimised, which is also when the entropy is maximised.

9 Availability

9.1 General Relation between C_P and C_V

For an ideal gas we showed that

$$C_P - C_V = nR.$$

We are now ready to find a general relation between C_P and C_V . At a constant volume from the first law we have $dU = dQ$ the central equation we have $dU = T dS$. Thus

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

At constant pressure we have $dH = dU = T dS$ and so

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

This suggests that we should work with the entropy, $S = S(T, V)$. In this case dS is given by

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV.$$

Differentiating with respect to temperature at constant pressure this becomes

$$\left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial T} \right)_P + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial S}{\partial T} \right)_V + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P.$$

Multiplying by T we have

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial V} \right)_T + T \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = C_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P.$$

We now introduce the isobaric thermal expansivity, β , defined as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P.$$

Thus

$$C_P = C_V + TV\beta \left(\frac{\partial S}{\partial V} \right)_T. \quad (9.1)$$

By Maxwell's relations we have

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

The triple product rule for partial derivatives is that

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1.$$

Using this and the reciprocal rule

$$\frac{1}{\left(\frac{\partial x}{\partial y} \right)_z} = \left(\frac{\partial y}{\partial x} \right)_z$$

we have

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

Introducing the isothermal bulk modulus, K , defined as

$$K = -V \left(\frac{\partial P}{\partial V} \right)_T$$

we have

$$\left(\frac{\partial S}{\partial V} \right)_T = -V \left(\frac{\partial P}{\partial V} \right)_T \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = K\beta.$$

Substituting this into equation 9.1 we have

$$C_P - C_V = TV\beta \left(\frac{\partial S}{\partial V} \right)_T = TV\beta^2 K = \frac{TV\beta^2}{\kappa}.$$

Here we have introduced the isothermal compressibility, $\kappa = 1/K$, which is more commonly used with gasses whereas K is more commonly used with solids. We see that

$$C_P - C_V \propto V$$

which makes sense as it is an extensive property meaning it depends on how much stuff there is. For all known substances $K > 0$ and also $T > 0$ in kelvins and $\beta^2 > 0$ for all β so $C_P - C_V \geq 0$ and $C_P \geq C_V$. This even works if the thermal expansion, β , is negative. This means that the difference is not due to the work done expanding at constant P as $C_P \geq C_V$ even if the material shrinks upon heating, this goes against one of the most common (incorrect) explanations for why C_P is greater. $C_P = C_V$ at the density maximum of water (which occurs at about 4°C and 1 atm). For solids and liquids β is usually small and therefore $C_P \approx C_V$. For this reason we often don't differentiate between C_P and C_V and just quote a single value of heat capacity, which is usually C_P .

9.2 Changes in Heat Capacities

The values of C_V and C_P , even for an ideal gas, depend on the structure of the molecules as the degrees of freedom are important. At room temperature however most vibrational degrees of freedom aren't accessible so only translational and rotational degrees of freedom play a part.

One thing that we might want to know is how does C_V change with volume. That is what is

$$\left(\frac{\partial C_V}{\partial V} \right)_T?$$

We can calculate this fairly easily:

$$\begin{aligned}\left(\frac{\partial C_V}{\partial V}\right)_T &= T \left(\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T} \right)_V \right)_T \\ &= T \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V} \right)_T \right)_V \\ &= T \left(\frac{\partial}{\partial T} \left(\frac{\partial P}{\partial T} \right)_V \right)_V \\ &= T \left(\frac{\partial^2 P}{\partial T^2} \right)_V.\end{aligned}$$

Here we have used one of Maxwell's relations:

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

Similarly we can show that

$$\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P.$$

We can obtain these derivatives directly from the equations of state without even needing to know C_V and C_P , for example an ideal gas has

$$V = \frac{nRT}{P} \implies \left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial}{\partial T} \left(\frac{\partial}{\partial T} \frac{nRT}{P} \right)_P \right)_P = \left(\frac{\partial}{\partial T} \frac{nR}{P} \right)_P = 0.$$

Sometimes we can measure

$$\left(\frac{\partial C_P}{\partial P} \right)_T$$

at multiple pressures and integrate to get C_P , or we could find C_V in a similar way.

One interesting point is that C_P is infinite at phase transitions as at a phase transition $\Delta T = 0$ between phases and $\Delta V \neq 0$. Hence

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = -P \left(\frac{\partial V}{\partial T} \right)_P$$

assuming an ideal gas so U is constant at a phase boundary since T is constant and $U = U(T)$. The latent heat is

$$L = \int_{T-\delta T}^{T+\delta T} C_P dT$$

where T is the temperature at which the phase transition occurs and $\delta T \rightarrow 0$. We know that L is finite and therefore we model C_P with a delta distribution at phase transitions.

9.3 Why Don't Experiments Work

Many classical physics experiments are based on the assumption that

$$F = -\frac{\partial U}{\partial x}.$$

While this is true under ideal conditions things like friction get in the way. We can quantify how much using thermodynamics. Differentiating the central equation with respect to volume and at constant temperature we have

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial T} \right)_T - P = T \left(\frac{\partial P}{\partial T} \right)_V - P = \frac{T\beta}{\kappa} - P.$$

Here we have used a Maxwell relation and the definitions of β and κ . Since pressure is force per unit area we can divide by area to get

$$\left(\frac{\partial U}{\partial x} \right)_T = \frac{T\beta}{\kappa A} - F \implies F = -\left(\frac{\partial U}{\partial x} \right)_T + \frac{T\beta}{\kappa A}.$$

This extra term compared to the definition of potential energy explains why many experiments don't give quite the expected value.

9.4 Energy Change with Pressure

The energy increases under a pressure change. We can show this by differentiation the central equation with respect to pressure and holding T constant:

$$\left(\frac{\partial U}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - P \left(\frac{\partial V}{\partial P}\right)_T = T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T$$

where we have used one of Maxwell's relations to get rid of S . Identifying various terms this is

$$\left(\frac{\partial U}{\partial P}\right)_T = -TV\beta + PV\kappa_T$$

where κ_T is the isothermal compressibility, defined as

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T.$$

We can show that

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}$$

where κ_S is the adiabatic compressibility, defined as

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S.$$

This gives us another link between thermal (C_P/C_V) and mechanical (κ_T/κ_S) properties.

9.5 Entropy of an Ideal Gas (Again)

The entropy per mole of an ideal gas is $s = s(T, V)$.

$$ds = \left(\frac{\partial s}{\partial T}\right)_V dT + \left(\frac{\partial s}{\partial V}\right)_T dV = c_V \frac{dT}{T} + \beta K dV.$$

This applies to any fluid so far. For an ideal gas we have that $\beta K = R/V$ and c_V is constant so integrating this we have

$$s = c_V \ln T + R \ln v + s_0.$$

Similarly we can show that

$$s = c_p \ln T - R \ln P + s_0.$$

So we have related changes in entropy to measurable properties via the equations of state.

9.6 Availability

Given a specific system how much work can we get out? The answer depends on the surroundings. Suppose that the system is surrounded by a T_0, P_0 reservoir. The second law means that

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0.$$

Which is

$$\Delta S_{\text{sys}} - \frac{\Delta Q}{T_0} \geq 0$$

where ΔQ is the heat transferred from the the surroundings to the system. The first law for the system means that $\Delta Q = \Delta U + P_0 \Delta V$ and hence

$$\Delta U + P_0 \Delta V - T_0 \Delta S \leq 0.$$

We define the availability, A , to be

$$A = U - T_0 S + P_0 V.$$

Note that this is different from the Gibbs free energy as T_0 and P_0 are the temperature and pressure of the surroundings, not the system.

A depends on the system and surroundings, $A = A(S, V, P_0, T_0)$. We have already seen that spontaneous changes in A are negative since

$$\Delta A = \Delta U + P_0 \Delta V - T_0 \Delta S \leq 0.$$

At equilibrium nothing can change and since ΔA can only decrease it must be minimised at equilibrium. In differential form

$$dA = dU - T_0 dS + P_0 dV.$$

At equilibrium we will have $T_0 = T$ and $P_0 = P$ and $dA = 0$. The following scenarios show how useful A is, at equilibrium by minimising A with certain conditions we have:

$T = T_0$	$P = P_0$	$A = U - TS + PV$	G minimised
$T = T_0$	V const	$A = U - TS + \text{const}$	F minimised
S const	V const	$A = U + \text{const}$	U minimised
S const	$P = P_0$	$A = U - \text{const} + PV$	H minimised
U const	V const	$A = \text{const} - T_0 S$	S maximised

A gives us a measure of how far we are from equilibrium.

The work, $P_0 \Delta V$ is used to push back the environment. It is wasted. The heat transferred could be used to run an engine producing useful work. We have

$$\Delta U = Q - W = Q - W_{\text{useful}} - P_0 \Delta V.$$

Q is the heat transported from the surroundings to the system. Rearranging this and substituting in $Q = T_0 \Delta S$ we have

$$0 = \Delta U + P_0 \Delta V - T_0 \Delta S + W_{\text{useful}} = W_{\text{useful}} - \Delta A.$$

Therefore the maximum amount of useful work that we can extract is

$$W_{\text{max}} = -\Delta A.$$

This occurs if and only if all changes are reversible. In all other cases the work that we can extract is less. In differential form we have

$$\begin{aligned} dW_{\text{useful}} &\leq -dA \\ &= -dU + T_0 dS - P_0 dV \\ &= -T dS + P dV + T_0 dS - P_0 dV \\ &= (T_0 - T) dS - (P_0 - P) dV \end{aligned}$$

so we see that the work we can do is directly related to the difference in pressure and temperature of the system and surroundings.

10 Free Expansion of a Real Gas

In section 3.4 we considered a gas expanding into a vacuum to twice its original volume in a rigid adiabatic container. We argued that these properties meant no work was done and no heat was transferred, therefore by the first law $dU = 0$. Then we looked at an ideal gas and said that $dU = 0$ implies $dT = 0$ since for an ideal gas $U = U(T)$ so if U is constant T must be also. Finally we defined the Joule coefficient

$$\mu_J = \left(\frac{\partial T}{\partial V} \right)_U$$

such that $dT = \mu_J dV$, which we found by expanding a differential of $T = T(V, U)$ and setting $dU = 0$. For an ideal gas $\mu_J = 0$ since $dT = 0$.

We now have enough thermodynamics to reconsider this problem for real gases. Since the container is adiabatic the entropy of the surroundings, S_0 , is constant, so $dS_0 = 0$. Since the container is rigid the volume of the surroundings, V_0 , is constant so $dV_0 = 0$. For the surroundings $dU = dQ + dW = 0$ since

no work is done and no heat is transferred. Turning now to the system we want to know how the change in volume effects the temperature. We want to know what

$$\mu_J = \left(\frac{\partial T}{\partial V} \right)_U$$

is since then we know that

$$dT = \left(\frac{\partial T}{\partial V} \right)_U dV = \mu_J dV.$$

Integrating this we have

$$\Delta T = \int_{V_i}^{V_f} \left(\frac{\partial T}{\partial V} \right)_U dV = \int_{V_i}^{V_f} \mu_J dV.$$

We can't directly measure U so we would like to get rid of it. To do this we use the partial derivative triple product:

$$\left(\frac{\partial T}{\partial V} \right)_U = - \left(\frac{\partial T}{\partial U} \right)_V \left(\frac{\partial U}{\partial V} \right)_T.$$

Identifying

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

and using the reciprocal rule for partial derivatives we have

$$\left(\frac{\partial T}{\partial V} \right)_U = - \frac{1}{C_V} \left(\frac{\partial U}{\partial V} \right)_T.$$

Differentiating the central equation with respect to V at constant T we get

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P.$$

Therefore

$$\mu_J = \left(\frac{\partial T}{\partial V} \right)_U = \frac{1}{C_V} \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right],$$

where we have used a Maxwell relation to get rid of the entropy. This allows us to calculate μ_J from the equation of state, $U = U(P, T)$. For an ideal gas

$$P = \frac{nRT}{V} \implies \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V} \implies T \left(\frac{\partial P}{\partial T} \right)_V = T \frac{nR}{V} = P$$

so $\mu_J = 0$, which is what we expected. Note that in general μ_J can be positive or negative.

We can also calculate μ_J for a slightly more realistic gas, in this case a Van der Waal's gas:

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT.$$

This can be expanded in powers of the number density in what is called a Virial expansion:

$$\begin{aligned} Pv &= RT \left[1 + \left(b - \frac{a}{RT} \right) \left(\frac{1}{v} \right) + b^2 \left(\frac{1}{v} \right)^2 + \dots \right] \\ &= RT \left[1 + \frac{B_2}{v} + \frac{B_3}{v^2} + \dots \right]. \end{aligned}$$

Here B_i are the temperature dependent Virial coefficients. We want to use this to estimate ΔT for a given ΔV . For this we need μ_J , we approximate it keeping only up to the second Virial coefficient and we have

$$\mu_J \approx - \frac{1}{c_V} \frac{RT}{v^2} \frac{dB_2}{dT}.$$

For argon $dB_2/dT = 0.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ so if the volume of a mole of argon doubles then the temperature change is approximately $\Delta T = -0.6 \text{ K}$.

10.1 Fridges

Fridges use this effect of gases cooling upon expansion to cool the refrigerant. Except that in a fridge this is done continuously by forcing gas through a porous plug which can also hold a pressure difference on either side. The system of interest here is a sample of gas that starts on one side of the plug and then ends up on the other side. We assume that the plug stays the same and so the surroundings have no entropy change. We also assume that the surroundings exert a constant external pressure, this is a reasonable assumption for continuous flow.

Since external pressure is constant enthalpy is the thermodynamic potential of choice. We consider a reversible isenthalpic process. The work done is

$$\Delta W = P_i V_i - P_f V_i$$

where V_i is the initial volume and P_i and P_f are the initial and final velocities respectively. Note that this is slightly different to the standard $p dV$ work as it is the pressure that is changing, not the volume.

For this continuous process every state between the initial and final state is visited along an isenthalp. Isenthalps are typically shaped to have some maximum temperature. The curve that connects the maximum temperatures is called the inversion curve. At higher pressures than that at which the maximum temperature occurs a volume change results in heating as the pressure drops so the temperature moves up towards the maximum (which is to the left on a (P, T) diagram). At lower pressures an increase in volume and therefore decrease in pressure still causes movement in the same direction but on the other side of the maximum so the temperature decreases. We can think of this being because at high pressures the molecules start to form intermolecular bonds which decreases the energy and so reducing the pressure increases the energy as these bonds start to break.

Since we are interested in changing P and conserving H we use $T = T(P, H)$ and expand the differential as

$$dT = \left(\frac{\partial T}{\partial P} \right)_H dP + \left(\frac{\partial T}{\partial H} \right)_P dH = \left(\frac{\partial T}{\partial P} \right)_H dP = \mu_{JK} dP.$$

Here μ_{JK} is called the Joule–Kelvin coefficient. The temperature change is then given by

$$\Delta T = \int_{P_i}^{P_f} \mu_{JK} dP.$$

We want to eliminate H from this as we can't measure it. We start by using the triple product and reciprocal rule for partial derivatives as well as recalling that $(\partial_T H)_P = C_P$:

$$\mu_{JK} = \left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial T}{\partial H} \right)_P \left(\frac{\partial H}{\partial P} \right)_T = - \frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T.$$

Recalling that in differential form the enthalpy is

$$dH = T dS + V dP$$

and differentiating with respect to P at constant temperature we have

$$\left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V$$

so

$$\mu_{JK} = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

where we have used a Maxwell relation to get rid of entropy. To make a good fridge we want to choose a material with a small heat capacity and that undergoes a large volume change for a small temperature change. We can approximate the temperature change for a given pressure change as follows

$$\left(\frac{\partial T}{\partial P} \right)_H = \mu_{JK} \implies \Delta T \approx \mu_{JK} \Delta P.$$

For an ideal gas

$$V = \frac{nRT}{P} \implies \left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \implies T \left(\frac{\partial V}{\partial T} \right)_P = T \frac{nR}{P} = V$$

and so $\mu_{JK} = 0$. In general μ_{JK} can be positive or negative.

We can find the inversion temperature, where expansion goes from a cooling process to a heating process, by noting that at this point $\mu_{JK} = 0$ as this is the maximum of an isenthalp in a (P, T) diagram. Not all isenthalps have a maximum, above a certain temperature expansion will always be a heating process. We can find the temperature by setting $\mu_{JK} = 0$ and then setting $P = 0$. This maximum inversion temperature is important as above this temperature a gas cannot be cooled by expansion. Some values of the maximum inversion temperature are given in table 10.1. At very low temperatures helium is

Gas	Maximum inversion temperature
Argon	723 K = 450 °C
Nitrogen	621 K = 348 °C
Hydrogen	205 K = -68 °C
Helium	51 K = -222 °C

Table 10.1: Maximum inversion temperatures

typically used as a refrigerant, not because it works well (it doesn't) but because it is one of the only gases that is still a fluid at only a few kelvin. The other problem with this is that since the maximum inversion temperature of helium is so low another refrigeration process has to be used above 51 K before the helium can be used.

Real fridges use a phase change to have a very large value of

$$\left(\frac{\partial V}{\partial T}\right)_P.$$

For this freon-12 (dichlorodifluoromethane) used to be the gas of choice as at 1 atm it boils at -29.8°C so in the slightly higher pressure that a refrigerant is stored at it boils at approximately the temperature we want the fridge to be. Unfortunately freon-12 is a chlorofluorocarbon (CFC) which, when released into the atmosphere, destroy the ozone layer and act as an incredibly efficient green house gas. For this reason use of freon-12 has been banned in many countries and alternatives are used.

10.2 Other Forms of Work

So far we have considered mostly gas processes. In these processes an overwhelming amount of the total work is work done expanding against a pressure. However different systems have other, more important, forms of work. Some examples are given in table 10.2.

10.2.1 Stretching a Rubber Band

The work done stretching a rubber band is

$$dW = \mathcal{F} dL - P dV$$

however $P dV \ll \mathcal{F} dL$ so we typically only consider

$$dW = \mathcal{F} dL.$$

We can use many results we have already derived by substituting L for V and $-\mathcal{F}$ for P . For example the following Maxwell relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \rightarrow \left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial(-\mathcal{F})}{\partial T}\right)_L = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_L.$$

System	Intensive Variable	Extensive Variable	Infinitesimal work on the system
Gas/fluid	Pressure, P	Volume, V	$-P dV$
Wire/rod	Tension, \mathcal{F}	Length, L	$\mathcal{F} dL$
Electric cell	Emf, \mathcal{E}	Charge, Z	$\mathcal{E} dZ$
Magnetic material	Induction, B_0	Magnetic moment, \mathcal{M}	$B_0 d\mathcal{M}$
Dielectric material	Electric field, E	Polarisation, \mathcal{P}	$E d\mathcal{P}$

Table 10.2: Alternative forms of work

Consider an isothermal stretch. In this process rubber molecules, which are long chains, become less tangled and align, this means there is more order so the entropy decreases. Therefore we expect $(\partial_L S)_T < 0$ and therefore we expect $(\partial_T \mathcal{F})_L$ to be negative as well. Using this Maxwell relation and also the triple product we have

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_L = \left(\frac{\partial \mathcal{F}}{\partial L}\right)_T \left(\frac{\partial L}{\partial T}\right)_\mathcal{F} < 0.$$

The first derivative is certainly positive as we must increase the force to increase the length. We conclude that the second derivative will be negative and rubber will have a negative coefficient of linear expansion:

$$\alpha_L = \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_\mathcal{F}.$$

So a rubber band stretched with a constant force will cool.

We can use this to make (a very bad) engine. We could heat a rubber band to make it contract and use this to do work, say lifting a mass, M . The heat that we input will be $Q = C_P \Delta T$. The work done is

$$W = Mg\Delta L = MgL\alpha_L \Delta T.$$

The efficiency is then

$$\eta = \frac{W}{Q} = \frac{MgL\alpha_L}{C_P}$$

This appears to increase with Mg , which cannot be as this would allow for infinite efficiency, which is forbidden by the second law. We conclude that α_L must decrease at least as fast as $1/Mg$. Using Maxwell's relations we have

$$\alpha_L = \frac{1}{L} \left(\frac{\partial S}{\partial \mathcal{F}}\right)_T.$$

We posit that for sufficiently large forces all the molecules are aligned and therefore there is no scope for decreasing entropy by stretching further. In fact further stretching will cause the molecules to start breaking increasing entropy. We have managed to discover some important information for what seems to be a purely mechanical system using only thermodynamic principles.

11 Thermodynamics and Electrodynamics

We can apply many thermodynamic ideas to electromagnetism. For example we can take the internal energy to be the energy stored in the electromagnetic fields. We can consider the radiation pressure, $\langle S \rangle / c$ where $\mathbf{S} = \mathbf{E} \times \mathbf{H}$ is the Poynting vector and c is the speed of light. If we consider a black body as a cavity containing radiation then the volume is crucial, as well as the temperature. We can consider a magnetic field, $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$ as being a sum of an extensive property, \mathbf{H} , and intensive property \mathbf{M} .

For simplicity we assume that $H \gg M$ and therefore $\mathbf{B} \approx \mu_0 \mathbf{H}$. The magnetic energy is then $-BM$. We also assume that the volume is constant, or at least close to it, and therefore we can ignore any work done to expand, $P dV$. Instead we define the work done to be the energy used to increase magnetisation:

$$dW = \mathbf{B} \cdot d\mathbf{M}.$$

The central equation is then

$$du = T ds + B dM.$$

We can find the Maxwell relations by substituting $-B$ for P and M for V , for example:

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \rightarrow \left(\frac{\partial B}{\partial S}\right)_M = \left(\frac{\partial T}{\partial M}\right)_S.$$

It is also common to define the **total energy**, e_{tot} , which is the magnetic equivalent of enthalpy:

$$H = U + PV \rightarrow e_{\text{tot}} = u - BM.$$

Taking derivatives this becomes

$$de_{\text{tot}} = du - B dM - M dB = T ds - M dB$$

where we have substituted the central equation for du in the last step. We can also do something similar for the other thermodynamic potentials.

11.1 Magnetic Cooling

For the rest of this section we will consider a process of magnetic cooling. The approximations that we make are

- The induced magnetisation is small so $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) \approx \mu_0\mathbf{H}$.
- The susceptibility is scalar so the magnetisation is parallel to the field:

$$\mathbf{B} \cdot \mathbf{M} = BM.$$

Generalisation to a tensor susceptibility is straight forward but tedious.

- Volume is constant so $dV = 0$ and crucially there is no $P dV$ work.

The equipartition theorem in classical mechanics states that all degrees of freedom have the same energy and that all excited degrees of freedom contribute to the energy. The important degree of freedom that is introduced when considering a magnetic field is the alignment of any magnetic moments. For example if we turn on a magnetic field then the magnetic moments will align causing a decrease in entropy.

There are many degrees of freedom that we may consider normally:

- Rotational degrees of freedom – important in polyatomic gases.
- Vibrational degrees of freedom – important when considering chemical bonds.
- Electronic degrees of freedom (ability of electrons to move about) – important when considering materials with delocalised electrons, such as metals or plasmas.
- Orientational degrees of freedom – important when considering long molecules, such as those in rubber.
- Magnetic degrees of freedom – important when considering materials in an external magnetic field.

All of these are quantised in some way by \hbar . Only excited degrees of freedom contribute to the entropy.

11.1.1 The Magnetic Cooling Process

A paramagnet (magnetises in an external field and then loses magnetisation after the field is removed) is placed in contact with a heat bath. An external magnetic field is applied isentropically. The total entropy must therefore be constant, however by applying a magnetic field magnetic moments align decreasing the magnetic entropy. Thus another form of entropy must increase to balance this. In this case the only form of entropy that can increase is the thermal entropy. The paramagnet is then removed from the heat bath and then the field is removed isentropically. The thermal entropy then returns back to being magnetic entropy cooling the magnet.

During the magnetisation process the magnet loses heat to the heat bath. If this process is done isothermally, as is the most efficient (but slowest) way to do it, then

$$\left(\frac{\partial Q}{\partial B}\right)_T = T \left(\frac{\partial S}{\partial B}\right)_T = T \left(\frac{\partial M}{\partial T}\right)_B$$

using a Maxwell relation in the last step. We can measure the properties in the right hand side of this. During the adiabatic/isenthalpic demagnetisation the temperature is reduced:

$$\left(\frac{\partial T}{\partial B}\right)_S = - \left(\frac{\partial T}{\partial S}\right)_B \left(\frac{\partial S}{\partial B}\right)_T = - \frac{T}{C_B} \left(\frac{\partial S}{\partial B}\right)_T$$

Here we have used the triple product rule for partial derivatives and then defined the heat capacity at constant B as

$$C_B = \left(\frac{\partial U}{\partial T}\right)_B = \left(\frac{\partial T}{\partial S}\right)_T,$$

which uses the derivative of the magnetic central equation at constant B . If we use a Maxwell relation and define the magnetic susceptibility to be $\chi = M/B$ then we have

$$\left(\frac{\partial T}{\partial B}\right)_S = - \frac{T}{C_B} \left(\frac{\partial M}{\partial T}\right)_B = - \frac{TB}{C_B} \left(\frac{\partial \chi}{\partial T}\right)_B. \quad (11.1)$$

We now use Curie's law of susceptibility at lower temperatures:

$$M = a \frac{B}{T} \iff \chi^{-1} = \frac{T}{a}$$

where a is the Curie constant that we can measure (this is normally denoted C but we don't want to confuse it with a heat capacity). This law was empirically created by Pierre Curie.

The Schottky non-magnetic heat capacity is

$$c_B(T, B = 0) = \frac{b}{T^2}$$

for some constant b . Thus at some non-zero field strength, B :

$$\begin{aligned} c_B(T, B) &= \frac{b}{T^2} + \int_0^B \left(\frac{\partial c_B}{\partial B} \right)_T dB \\ &= \frac{b}{T^2} + \int_0^B T \left(\frac{\partial^2 M}{\partial T^2} \right)_B dB \\ &= \frac{b}{T^2} + \int_0^B T \frac{2aB}{T^3} dB \\ &= (b + aB^2) \frac{1}{T^2} \end{aligned}$$

Where we have used that

$$\left(\frac{\partial C_B}{\partial B} \right)_T = T \left(\frac{\partial^2 M}{\partial T^2} \right)_B,$$

which is the magnetic analogue of

$$\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P$$

which we have shown in section 9.2. We then wrote M using Curie's Law. Using this and Curie's law in equation 11.1 we have

$$\begin{aligned} \left(\frac{\partial T}{\partial B} \right)_S &= -BT \frac{T^2}{b + aB^2} \left(\frac{\partial}{\partial T} \frac{a}{T} \right)_B \\ &= -BT \frac{T^2}{b + aB^2} \frac{(-a)}{T^2} \\ &= \frac{aBT}{b + aB^2} \\ \implies \int \frac{dT}{T} &= \int \frac{aB}{b + aB^2} dB \\ \implies \ln \left(\frac{T_f}{T_i} \right) &= \frac{1}{2} \ln \left(\frac{b + aB_f^2}{b + aB_i^2} \right) \\ \implies T_f &= T_i \sqrt{\frac{b + aB_f^2}{b + aB_i^2}} \end{aligned}$$

We see that each cycle T is decreased by a fixed fraction. This means that we cannot get to $T = 0$ with a finite number of cycles.

Another issue is that Curie's law diverges at $T = 0$. A more accurate set of measurements reveals that

$$\chi = \frac{a}{T - T_C}$$

where T_C is the Curie temperature. Below T_C a paramagnet will spontaneously magnetise as there is no longer enough thermal energy to disrupt the alignment of magnetic moments. We can use this and perform the same analysis above with the substitution that $T \rightarrow T - T_C$ and we get

$$T_f = T_C + (T_i - T_C) \sqrt{\frac{b + aB_f^2}{b + aB_i^2}}$$

so we see that even after an infinite number of cycles the temperature cannot go below T_C . There is also a balance that needs to be struck. A weaker paramagnet will have a lower value of T_C so allows for more cooling but this cooling will occur much slower than if we use a stronger paramagnet which will have a higher value of T_C .

12 Thermal Radiation

In this section we will consider a system consisting of radiation in a cavity. The surroundings are the cavity walls which act as a heat bath at temperature T , as well as providing a fixed volume. Because of this we express U as a function of temperature and volume, $U = U(T, V)$. It can be shown that the pressure is $P = u/3$ where u is the energy per unit volume (not the energy per mole as lowercase usually denotes). This can be shown by considering kinetic theory with the Maxwell-Boltzmann distribution with $v = c$ for all particles, or as a consequence of relativity or with electromagnetism.

We split the cavity into two halves, A and B , with a small gap in the barrier. In the most general case the walls of both sides of the cavity can be made of different materials. The two sides are in thermal equilibrium and also due to the ability to exchange matter between the sides they are also at the same pressure. This means that $u_A = u_B$ since there is no heat flow. Therefore the Clausius statement of the second law means that we must have $u(T, V) = u(T)$.

We consider a different system for each wavelength of light. This is like replacing the gap with a filter that only allows one wavelength through. The same argument as above means that heat flows between the two sides until equilibrium is reached and the temperature, pressure, and internal energy per unit volume is the same on both sides. The internal energy per volume at wavelength λ is $u_\lambda(T)$ which is a thermodynamic function of T for some given value of λ . The form of this function will be the same for all λ . We know that at high temperatures things glow visibly and at slightly lower temperatures they glow in the infrared part of the spectrum. The peak of u_λ must therefore move with temperature. The total internal energy per unit volume is simply

$$u = \int_0^\infty u_\lambda(T) d\lambda.$$

Using the central equation we have

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

where we have used a Maxwell relation in the last step. Substituting in $P = u/3$, $U = uV$ and $u = u(T)$ we have

$$\left(\frac{\partial}{\partial V} uV\right)_T = u = T \left(\frac{\partial}{\partial T} \frac{u}{3}\right)_V - \frac{u}{3} = \frac{T}{3} \frac{du}{dT} - \frac{u}{3} \implies 4u = T \frac{du}{dT}.$$

Solving this we have

$$4 \ln T = \ln u + \ln k$$

for some constant, k . Rearranging we have

$$T^4 = ku.$$

Applying boundary conditions we find that

$$u(T) = \frac{4\sigma}{c} T^4$$

where c is the speed of light and $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is Stefan's constant which is related to by the flux, the flux is given by $uc/4 = \sigma T^4$. The fact that the exponent is 4 will lead to terms like $P = u/3$ when we integrate. This is a direct consequence of living in three dimensions where the velocity is split equally amongst the three directions leading to $1/3$ of the energy contributing to pressure in each direction.

We can get other thermodynamic quantities in terms of u as well. For example, the heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial}{\partial T} uV\right)_V = 4\sigma_0 V T^3$$

where $\sigma_0 = 4\sigma/c = 7.566 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}$ is the radiation constant. As well as this we can find the state variables such as entropy of the system:

$$S = \int \frac{C_V dT}{T} = \frac{4}{3}\sigma_0 VT^3,$$

the enthalpy:

$$H = U + PV = \frac{4}{3}\sigma_0 VT^4 = TS,$$

and the Gibbs free energy:

$$G = U - TS + PV = uV - TS + PV = \sigma_0 VT^4 - \frac{4}{3}\sigma_0 VT^4 + \frac{1}{3}VT^4 = 0.$$

This means that photons have zero Gibbs free energy. This is because photons appear and disappear and therefore must have $G = 0$ for this to be allowed so that G is constant if a photon appears/disappears.

The energy distribution looks like a slightly asymmetric bell curve (but is not normally distributed). We can fit power laws to the tails. For long wavelengths

$$u_\lambda \propto T\lambda^{-4}$$

and for short wavelengths

$$u_\lambda \propto \lambda^{-5} e^{-k/\lambda T}$$

for some constant k . It can also be shown that the wavelength that maximises u_λ is

$$\lambda_{\text{peak}} = \frac{1}{T} \cdot 2.898 \times 10^{-3} \text{ m}.$$

Note that this maximises the energy per unit volume, not the energy per photon, clearly $\lambda \rightarrow 0$ ($f \rightarrow \infty$) maximises the energy per photon, the reason that this is not the same is because u_λ takes into account the number of photons of wavelength λ . As well as this we know that

$$u(T) = \int_0^\infty u_\lambda(T) d\lambda.$$

Integrating the black body equation of state we get Stefan's law:

$$u(T) = \int_0^\infty u_\lambda(T) d\lambda = \frac{4\sigma}{c} T^4,$$

we then also require that

- $u_\lambda(T)$ decays as λ^{-5} for large values of λ ,
- $u_\lambda(T)$ doesn't blow up for high frequencies (low λ),
- $u_\lambda(T)$ gives the same temperature,

$$T = \left(\frac{\partial u_\lambda}{\partial s_\lambda} \right)_V,$$

for all values of λ .

Using this we can come up with an exact form for $u_\lambda(T)$. Planck discovered that it is easier to relate u and s than u and T so that is what we will do here. Planck started with

$$\left(\frac{\partial s}{\partial u} \right)_V = \frac{1}{T},$$

which comes from the third condition on $u_\lambda(T)$ above. From this we know that

$$\left(\frac{\partial^2 s}{\partial u^2} \right)_V = \left(\frac{\partial(1/T)}{\partial} \right)_u V.$$

At long wavelengths we want

$$\left(\frac{\partial(1/T)}{\partial u} \right)_V \propto -\frac{1}{u^2},$$

and at short wavelengths we want

$$\left(\frac{\partial(1/T)}{\partial u}\right)_V \propto -\frac{1}{u}.$$

The simplest way to combine these two conditions is

$$\left(\frac{\partial(1/T)}{\partial u}\right)_V = \left(\frac{\partial^2 s}{\partial u^2}\right)_V = \frac{C_1}{u(u + C_2)}$$

for some constants C_1 and C_2 . Integrating this we have

$$\frac{1}{T} = \int \frac{C_1}{u(u + C_2)} du = \frac{C_1}{C_2} \ln \left(\frac{u}{u + C_2} \right).$$

Rearranging this and reintroducing λ we have

$$u_\lambda(T) \propto \lambda^{-5} \left(\frac{1}{e^{k/\lambda T} - 1} \right).$$

This fits the data perfectly.

A geometric series of the form $1 + r + r^2 + r^3 + \dots$ can be shown to sum to

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1 - r},$$

if $|r| < 1$. Using this we see that

$$u_\lambda(T) \propto \sum_{n=0}^{\infty} e^{-nk/\lambda T} = \sum_{n=0}^{\infty} e^{-nhc/\lambda k_B T}$$

where we use $k = hc/k_B$. This shows that $u_\lambda(T)$ follows the Boltzmann distribution with $E = nch/\lambda = nhf$. This assumes discrete energy levels quantised by $nhf = nhc/\lambda$. With these constants we also have

$$\sigma = \frac{2\pi^5 k_B^4}{15h^3 c^2}.$$

13 Phase Diagrams

A phase diagram shows the different phases (states) of matter on some set of axes. The simplest phase diagram is for an ideal gas, since an ideal gas, by definition, is always a gas under any conditions, so the phase diagram is simply one phase, ‘gas’, everywhere.

A real phase diagram is more complicated. Mathematically this is because, at a phase boundary, the equations of state are in general

- not analytic,
- not continuous,
- not differentiable.

This makes mathematics at phase boundaries really hard. Phase diagrams can be of any dimensionality. For example for pure water the equation of state is in three-dimensional (P, V, T) -space. This means that given two state variables we can find the third from the equation of state. The phases are separated by curves one dimension down from the dimension of the equation of state, so in the case of water phases are separated by two-dimensional surfaces. We can fix one variable, for example if we work at room temperature then the equation of state at room temperature is simply a plane through the equation of state and the phases are now separated by lines in one dimension.

For a physics perspective within a phase we expect that the equation of state will be nice (by this we mean analytic, continuous, and differentiable) since it would be non-physical to have, for example, an instantaneous change of volume by some finite-amount. However at the boundaries, say between liquid and gas, we can have such sudden expansions as the liquid vaporises and increases rapidly in volume.

We label each region of the phase diagram with the phase that is stable at that point. This is the phase with the lowest Gibbs free energy at this point. Sometimes phases can coexist. For example above the critical temperature water can be a liquid or gas and will spontaneously boil. This means that liquid is not stable at this point.

Since low Gibbs free energy is favoured and $G = U - TS + PV$ higher temperatures favour higher entropies, for example gasses, whereas higher pressures favour higher densities (i.e. lower volumes), for example solids.

Some important features of phase diagrams are given here:

- The equilibrium point between two phases is where the free energy is minimised.
- Conjugate variables are those which appear together in free energy equations, for example P and V are conjugate, as are T and S . Typically derivatives involving conjugate variables must be positive, for example $\partial P/\partial V > 0$, or equivalently the bulk modulus is positive, as if this were not the case then the free energy could be spontaneously decreased by volume collapse and everything would shrink to nothingness. Similarly $\partial S/\partial T > 0$, or equivalently the heat capacity is positive.
- A triple point is where solid, liquid, and gas coexist. These are unique points on a two dimensional phase diagram. For example the triple point of water is at approximately 273.1575 K (0.0075 °C) and 611.657 Pa (0.006 037 atm).
- A sublimation line is the solid-gas boundary. A substance crossing this point will move between solid and gas without ever becoming liquid. For example at room temperature and pressure solid carbon dioxide will sublime, this is the reason that dry ice is dry.

At a phase boundary two parts of a system, one part for each phase, are in equilibrium. This means that P and T are constant throughout the system. The relevant potential is then the Gibbs free energy, $dG = V dP - S dT$. A system in mechanical (pressure) and thermal (temperature) equilibrium minimises the Gibbs free energy. For an irreversible process $dG < 0$ and for a reversible process $dG = 0$. If instead T and V were in equilibrium then the relevant potential would be the Helmholtz free energy, $dF = -P dV - S dT$.

13.1 Forbidden Properties

We can show that some properties are thermodynamically impossible (i.e. they violate the second law). For example the bulk modulus,

$$K_S = -V \left(\frac{\partial P}{\partial V} \right)_S,$$

is always positive. Consider the system split into two parts, A and B , by a constant S and V boundary. If A grows by ΔV then B must shrink by ΔV . Thus Taylor expanding

$$\Delta U_A = \left(\frac{\partial U}{\partial V} \right)_S \Delta V + \left(\frac{\partial^2 U}{\partial V^2} \right)_S \frac{(\Delta V)^2}{2} + \mathcal{O}((\Delta V)^3).$$

Similarly

$$\Delta U_B = - \left(\frac{\partial U}{\partial V} \right)_S \Delta V + \left(\frac{\partial^2 U}{\partial V^2} \right)_S \frac{(\Delta V)^2}{2} - \mathcal{O}((\Delta V)^3).$$

So the total energy change is

$$\Delta U = \Delta U_A + \Delta U_B = \left(\frac{\partial^2 U}{\partial V^2} \right)_S (\Delta V)^2 + \mathcal{O}((\Delta V)^4) = -V \left(\frac{\partial P}{\partial V} \right)_S \frac{(\Delta V)^2}{V}.$$

This last part comes from differentiating the central equation with respect to volume. By the second law U is minimised at equilibrium so $dU > 0$. Volume, V , and $(\Delta V)^2$ are both positive quantities. This means that

$$K_S = \frac{V \Delta U}{(\Delta V)^2} > 0.$$

Similarly if we consider the same system at constant volume then

$$dU = dU_A + dU_B = \left(\frac{\partial^2 U}{\partial S^2} \right)_V (\Delta S)^2 = \frac{1}{T} \left(\frac{\partial T}{\partial S} \right)_V T (\Delta S)^2 = \frac{T (\Delta S)^2}{c_V}.$$

Since $dU, T, (\Delta S) > 0$ we must also have that $c_V > 0$.

13.2 Coexisting Phases

Suppose we have a system that has two coexisting phases. For example ice in water. The total Gibbs free energy, G is

$$G = g_1 M_1 + g_2 M_2$$

where g_i and M_i are the Gibbs free energy and mass of the relevant phase. Since mass is conserved $dM_1 = -dM_2$. Minimising G at equilibrium we have $dG = 0$ so

$$dG = g_1 dM_1 + g_2 dM_2 = (g_1 - g_2) dM_1 = 0.$$

This means that $g_1 = g_2$. So two phases can coexist if they have the same Gibbs free energy. Conversely if $g_1 > g_2$ then material will transfer from phase 1 to phase 2 until equilibrium is reached. The fact that there are three variables of interest, (P, V, T) , and two constraints, the equation of state and $g_1 = g_2$, means that the coexistence can happen only along a line in (P, T) -space.

If instead a system is at constant T and V then we minimise the Helmholtz free energy, $F = U - TS$ meaning that $dF = P dV - S dT = 0$ at equilibrium. Our constraint is then $V = \nu_1 M_1 + \nu_2 M_2$ where ν_i is the density of the relevant phase. Typically this will lead to multiple lines, one for each phase. These lines can be linked by a common tangent line in (V, F) -space, the gradient of which gives the pressure at coexistence:

$$\left(\frac{\partial F}{\partial V} \right)_T = P.$$

Notice that $f_1 \neq f_2$ necessarily at equilibrium. Compression occurs when material transfers to a denser phase. Along an isotherm ($dT = 0$) at coexistence ($dG = 0$) is

$$dP = \frac{1}{V} (dG + S dT) = 0.$$

So pressure is constant along the coexistence line. This means that material can compress without changing pressure at this point which means that the isothermal compressibility at a phase boundary is infinite.

13.3 Van der Waal's Gas Phase Diagram

Van der Waal's equation of state can be written as

$$Pv^3 - (Pb + RT)v^2 + av - ab = 0$$

where $v = V/n$ is the volume per molecule and n is the number of molecules in the sample. This is a cubic which means that in general $v(P, T)$ is multi-valued. The critical point occurs when the three roots of this cubic coincide. It can be shown that the critical point occurs at

$$vu_C = 3b, \quad P_C = \frac{a}{27b^2}, \quad \text{and} \quad T_C = \frac{8a}{27Rb}.$$

For $T > T_C$ $v(P, T)$ is single valued. The Boyle temperature,

$$T_B = \frac{a}{Rb} = \frac{27}{8} T_C$$

is the point when a Van der Waal's gas behaves most like an ideal gas. At lower temperatures inter-molecular forces become important, characterised by a , and at higher temperatures the volume of the molecules becomes important, characterised by b .

We can rewrite the Van der Waal's equation in a dimensionless form using the critical point:

$$\left(\frac{P}{P_C} + \frac{3}{(v/v_C)^3} \right) \left(3 \frac{v}{v_C} - 1 \right) = 8 \frac{T}{T_C}.$$

13.3.1 Maxwell's Construction

To deal with the multi-valued nature of an isotherm Maxwell replaced the problem part of the isotherm with a straight line such that the area below the line and above the isotherm is equal to the area above the line and below the isotherm. This essentially flattens out the curvy part of the cubic in a way that keeps $dG = 0$ since integrating the density along the isotherm with respect to the pressure gives the area between the line and the isotherm and is zero if the line is constructed properly. This is shown in figure 13.1.

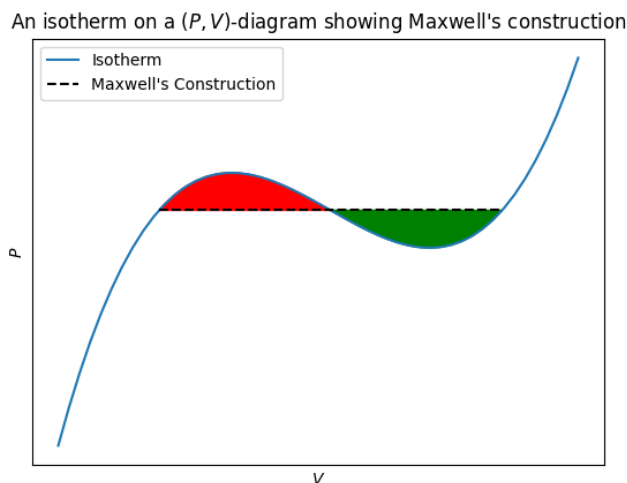


Figure 13.1: A (P, V) -diagram showing an isotherm for a Van der Waal's gas as well as Maxwell's construction. The two shaded areas are equal.

14 More Phase Diagrams

14.1 More Forbidden Properties

In the last section we saw that applying the second law to conjugate variables P and V , and T and S that K_S , the bulk modulus, and C_V , are always positive. We showed this by considering the change in U of a two part system. If instead of U we consider F and the conjugate variables P and V then we find that $K_T > 0$. If instead of U we consider H and the conjugate variables T and S then we find that $C_P > 0$.

This only applies for conjugate variables, for example there is no equivalent restriction on dV/dT , we know this because water below 4°C will contract as it cools whereas water above 4°C will expand. This means that depending on the temperature dV/dT can be positive or negative.

We can view these restrictions as an application of the central equation, $dU = T dS - P dV$, and the second law of thermodynamics. We cannot increase T and S at the same time as this would cause a spontaneous increase in dU , which is forbidden by the second law. In general if a bulk modulus, K , is negative then this would allow for heat to transfer to work, this violates the Kelvin–Planck statement of the second law. Similarly if a heat capacity, C , is negative then it would be possible to move heat from cold to hot, this violates the Clausius statement of the second law.

14.2 Stress and Strain

Stress, σ_{ij} , and strain, ε_{ij} , are three-dimensional second-order tensors related by the three-dimensional fourth order elasticity tensor, C_{ijkl} , by the equation

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}.$$

σ_{ij} and ε_{kl} are conjugate variables but they can be negative as long as the eigenvalues of C_{ijkl} are positive. For example pulling a bar along the x -axis will cause its length to increase along the x -axis but

its width along the y and z axes will decrease. The net effect however will be an increase. The elastic energy is

$$\frac{1}{2} C_{ijkl} \varepsilon_{ij} \varepsilon_{kl}$$

and this must be positive so no matter what the signs of ε_{kl} and C_{ijkl} (and hence the signs of σ_{ij}) the signs must combine in such a way that the energy is positive.

14.3 Phase Boundary Slope

Consider a (T, P) -phase diagram. We know that along a phase boundary separating phases 1 and 2 we must have that the Gibbs free energy is equal for both phases, $g_1 = g_2$. Consider two points on the phase boundary, (T, P) and $(T + dT, P + dP)$. Since both points are on the phase boundary we must have

$$g_1(T, P) = g_2(T, P), \quad \text{and} \quad g_1(T + dT, P + dP) = g_2(T + dT, P + dP).$$

If we Taylor expand the second condition then we find that

$$g_1(T, P) + \left(\frac{\partial g_1}{\partial T} \right)_P dT + \left(\frac{\partial g_1}{\partial P} \right)_T dP + \dots = g_2(T, P) + \left(\frac{\partial g_2}{\partial T} \right)_P dT + \left(\frac{\partial g_2}{\partial P} \right)_T dP + \dots.$$

Noting that $g_1(T, P) = g_2(T, P)$ appears on both sides so cancels and then rearranging we have

$$\left[\left(\frac{\partial g_1}{\partial T} \right)_P - \left(\frac{\partial g_1}{\partial T} \right)_T \right] dT = \left[\left(\frac{\partial g_2}{\partial P} \right)_T - \left(\frac{\partial g_1}{\partial P} \right)_T \right] dP.$$

Now using $dg = v dP - s dT$ we get

$$\left(\frac{\partial g}{\partial T} \right)_P = -s, \quad \text{and} \quad \left(\frac{\partial g}{\partial P} \right)_T = v.$$

Hence

$$\begin{aligned} [-s_1 + s_2] dT &= [v_2 - v_1] dP \\ \implies \left(\frac{\partial P}{\partial T} \right)_{\text{pb}} &= \frac{s_2 - s_1}{v_2 - v_1} = \frac{S_2 - S_1}{V_2 - V_1} \end{aligned}$$

where pb indicates the derivative is computed at the phase boundary. We can rewrite this using the latent heat, $\ell = T(s_2 - s_1)$, which gives

$$\left(\frac{\partial P}{\partial T} \right)_{\text{pb}} = \frac{\ell}{T(v_2 - v_1)} = \frac{\ell}{T(V_2 - V_1)}.$$

This is the **Clausius–Clapeyron equation**. The latent heat, ℓ , is positive for a phase transition from a lower temperature phase to a higher temperature phase. Suppose that the lower temperature phase is solid and the higher temperature phase is liquid. If $v_2 > v_1$ then

$$\left(\frac{\partial P}{\partial T} \right)_{\text{pb}} > 0$$

so the solid expands upon melting (most solids). If instead $v_2 < v_1$ then

$$\left(\frac{\partial P}{\partial T} \right)_{\text{pb}} < 0$$

so the solid contracts upon melting (e.g. water). So the gradient of the solid–liquid phase boundary will be positive on a (T, P) -diagram if the solid expands upon melting will be negative if the solid contracts upon melting.

14.4 Boiling Point

Let v_v be the specific vapour volume (i.e. the volume of one mole of vapour) and v_l be the specific liquid volume. Typically $v_v \gg v_l$ and therefore we can approximate $v_v - v_l \approx v_v$. For an ideal gas

$$v_v = \frac{RT}{P}.$$

The Clausius–Clapeyron equation then becomes

$$\left(\frac{\partial P}{\partial T}\right)_{\text{pb}} = \frac{\ell}{T(v_v - v_l)} \approx \frac{\ell}{Tv_v} = \frac{\ell}{T} \frac{P}{RT} = \frac{\ell P}{RT^2} \implies \frac{1}{P} \left(\frac{\partial P}{\partial T}\right)_{\text{pb}} = \frac{\ell}{RT^2}.$$

We assume that ℓ is approximately constant over the range of interest and integrate this. We get

$$\ln P = -\frac{\ell}{RT} + C$$

for some constant of integration, C . From this we can see that the boiling point changes linearly with $\ln P$. For example at sea level is 100°C , where the pressure is 0.031 MPa whereas at the top of mount Everest the pressure is only 0.031 MPa (0.31 atm) and water boils at 70°C . This makes it impossible to make good tea up a mountain as the water can't be heated above 70°C without a pressurised vessel.

We can be more precise if we use Trouton's rule, that the entropy of vaporisation is $10.5R$ and the latent heat is $\ell = 10.5RT_{\text{vap}}$, which is not constant as the boiling point, T_{vap} , depends on the pressure. The molar entropy of liquids at the boiling point is the same (or similar) for all liquids. This is because at this point the entropy due to possible molecular arrangements dominates and other effects, such as the entropy of individual molecules, can be ignored. We can measure the enthalpy using the fact that $g = h - Ts$ and $\Delta g = 0$ across a phase boundary, which means that

$$\Delta h_{\text{vap}} = T_{\text{vap}} \Delta s_{\text{vap}}.$$

Therefore the Clausius–Clapeyron equation becomes

$$\left(\frac{\partial P}{\partial T}\right)_{\text{pb}} \approx \frac{\ell}{T} \frac{P}{RT} \approx \frac{10.5P}{T} \implies \frac{P}{P_0} \approx \left(\frac{T}{T_0}\right)^{10.5},$$

where P_0 and T_0 are constants to be determined.

14.5 Slopes and Discontinuities

The plot of g on a (T, P) -diagram will always have a negative slope as

$$\left(\frac{\partial g}{\partial T}\right)_P = -s < 0.$$

The slope is steeper for higher temperatures meaning that at higher temperature phases will have lower Gibbs free energy. For example a vapour will have a lower Gibbs free energy than a liquid at temperatures higher than the boiling point (they have the same Gibbs free energy at the boiling point). This makes sense as we defined the stable phase (which at temperatures higher than the boiling point is the vapour) as the phase with the lowest Gibbs free energy. The slope is steeper at higher T as

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_P = -\left(\frac{\partial s}{\partial T}\right)_P = -\frac{c_P}{T} < 0.$$

If T_0 is the melting point and we have a liquid, l , phase and solid, s , phase then $g_l(T_0) = g_s(T_0)$ so for $T < T_0$ we will have $g_s(T) < g_l(T)$ and vice versa.

There will be a discontinuity in the entropy at T_0 :

$$\Delta s = -\Delta \left(\frac{\partial g}{\partial T}\right)_P$$

and since $s_l > s_s$ we expect that $\Delta s \neq 0$.

Similar logic will tell us that $g(P)$ is continuous across a transition and has a discontinuity in its slope at P_0 :

$$\Delta v = -\Delta \left(\frac{\partial g}{\partial P} \right)_T$$

and since we expect a finite volume change when the phase changes there is no reason for the slope to be continuous.

Consider the following:

$$\left(\frac{\partial(G/T)}{\partial T} \right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2} = \frac{G + TS}{T^2} = -\frac{H}{T^2}.$$

Integrating then gives

$$\int_1^2 d \left(\frac{G}{T} \right) = \frac{G_2}{T_2} - \frac{G_1}{T_1} = - \int_1^2 \frac{\langle H \rangle}{T^2} dT.$$

Since P , V , T , U , and H are all only dependent on the positions of molecules and on their velocities we can compute these values with a simulation or a lot of quantum mechanics. The variables S , F , and G cannot be directly computed from observed values.

15 The Third Law of Thermodynamics

What is the entropy at $T = 0$ K? Previously we defined the entropy as

$$S = \int_0^T \frac{dQ}{T} + S_0.$$

Thus at $T = 0$ K $S = S_0$ so unless S_0 is known the absolute entropy is not a meaningful quantity. This is why we work with differences in entropy and ratios of entropies.

15.1 Nernst's Statement of the Third Law

The Nernst heat theorem is

Consider a system undergoing a process between initial and final equilibrium states as a result of external influences, such as pressure. The system experiences a change in entropy. This change tends to zero as the temperature characterising the process tends to zero.

—W. Nernst

What this says is that $\Delta S \rightarrow 0$ as $T \rightarrow 0$.

This is backed up by experimental evidence. For any exothermic isothermal chemical process ΔH increases with temperature and ΔG decreases with temperature. Nernst posited that at $T = 0$ $\Delta G = \Delta H$ meaning

$$\begin{aligned} \Delta G &= G_f - G_i \\ &= \Delta H - \Delta(ST) \\ &= H_f - H_i - T(S_f - S_i) \\ &= \Delta H - T\Delta S \end{aligned}$$

So by the observation that

$$\lim_{T \rightarrow 0} \frac{d}{dT} (\Delta H - \Delta G) = 0$$

we have

$$0 = \lim_{T \rightarrow 0} \left[\frac{d}{dT} \Delta H - \frac{d}{dT} \Delta H + \frac{d}{dT} (T\Delta S) \right] = \lim_{T \rightarrow 0} \frac{d}{dT} (T\Delta S) = \lim_{T \rightarrow 0} \Delta S$$

The fact that $\Delta S \rightarrow 0$ as $T \rightarrow 0$ is a statement of the **third law of thermodynamics**.

15.2 Planck's Statement of the Third Law

Max Planck stated the third Law as

The entropy of all perfect crystals is the same at absolute zero and may be taken to be zero.

—M. Planck

This comes in two parts:

1. All perfect crystals have the same entropy because to be a perfect crystal is to have no disorder.
2. With no other constraints we are free to choose $S_0 = 0$.

This is supported by experimental evidence. As well as this if we look at the statistical definition of entropy,

$$S = k_B \ln W,$$

we see that since there is only one way to make a perfect crystal since we take atoms to be indistinguishable so permuting different atoms doesn't make a different crystal, only moving atoms which introduces defects, we have $S = k_B \ln 1 = 0$.

15.3 Simon's Statement of the Third Law

Sir Francis Simon stated the third law as

The contribution to the entropy from each aspect of a system which is in thermodynamic equilibrium disappears at absolute zero.

—F. Simon

That is the configurational entropy, vibrational entropy, magnetic entropy, etc. all vanish as $T \rightarrow 0$.

15.4 Vanishing Heat Capacity

Consider the heat capacity,

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

We can then use that

$$dT \ln T = \frac{1}{T} \implies d \ln T = \frac{dT}{T}$$

to get

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

Thus letting $T \rightarrow 0$ we have $\ln T \rightarrow -\infty$, and by the third law $\Delta S \rightarrow 0$. This means that there are no constraints on $\Delta \ln T$, importantly $\Delta \ln T \neq 0$ so $C_V \rightarrow 0$.

This is true for all materials and all heat capacities (C_P , C_B , etc. all tend to zero for any material as $T \rightarrow 0$). From this we can see that the ideal gas heat capacities, such as $C_V = 3R/2$, fail at low T as they do not vanish. The Schottky heat capacity, $C_B(T, B = 0) = b/T^2$ also fails at low temperatures. This means that Curie's law fails at low temperatures. This means that there cannot be paramagnets at $T = 0$. This is because if there are magnetic moments then as T decreases eventually the magnetic moments overcome thermal effects and align to form permanent magnets at low temperatures.

15.5 Vanishing Thermal Expansion Coefficients

Consider the thermal expansion coefficient,

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T \approx -\frac{1}{V} \frac{\Delta S}{\Delta P}$$

where we have used a Maxwell relation in the second equality. As $T \rightarrow 0$ $\Delta S \rightarrow 0$ so $\beta \rightarrow 0$. Again this is true for any material.

15.6 Vanishing Slope of the Phase Boundary

Consider the Clausius–Clapeyron equation:

$$\left(\frac{\partial P}{\partial T}\right)_{\text{pb}} = \frac{\Delta S}{\Delta V}.$$

Clearly this tends to zero as $T \rightarrow 0$. Therefore all phase boundaries have zero slope at $T = 0$. This has been experimentally observed.

15.7 Quantum Statement of the Third Law

Consider the statistical definition of entropy, $S = k_B \ln W$. A quantised, finite, amount of energy is needed to leave the ground state. The ground state in this context being the state corresponding to $W = 1$, which is a perfect crystal. An infinitesimal temperature change cannot provide this finite amount of energy/ Therefore the infinitesimal processes at $T = 0$ cannot change W .

The third law really comes into effect when $k_B T$ is on a similar scale to the quantisation energy. Above this temperature there is enough energy that the third law is not particularly important. For a diatomic gas $C_V = 5R/2$ under standard conditions. This is because the vibrational states are inaccessible at room temperature as the vibrational quantisation is of a similar scale to $k_B T$ when T is room temperature. Thus the third law means that the vibrational entropy is zero at room temperature.

For a metal at a low temperature $c_V \approx c_P = aT + bT^3$. We can associate aT with the conduction of electrons and bT^3 with the lattice vibrations. Using

$$\frac{c_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V = a + bT^2$$

and integrating we have

$$S(T) = aT + \frac{1}{3}bT^3.$$

Both contributions clearly tend to zero as $T \rightarrow 0$. This corresponds to all electron states below the Fermi energy being occupied and all lattice vibrations (which we model as quantum harmonic oscillators) being in the ground state. The contribution of this non-zero zero point energy means that the Debye law, that $c_V \propto T^3$, is not quite correct.

15.8 Zeno's Paradox Statement of the Third Law

Zeno's paradox is the idea that it is impossible to do something because to do it we must first do half of it and to do half of it we must first do a quarter of it and so on for an infinite number of steps. This isn't usually true but it is when it comes to the third law. We can state the third law as

It is impossible to reach absolute zero in a finite number of processes.

We saw this when we considered magnetic cooling.

15.9 Glasses

It looks like the entropy of a glass doesn't go to zero as $T \rightarrow 0$. This is because a glass will still have entropy due to disorder. Decreasing the temperature only decreases the vibrational energy. From this we conclude that glasses aren't in equilibrium and over time we expect a glass to crystallise.

15.10 Statistical Consideration

A **microstate** is a possible arrangement of particles at a given instant in a given phase. A **macrostate** is a group of microstates which correspond to the same thermodynamic quantities, such as P , V , T , etc. **Ergodicity** means that it is possible to move between microstates. **Equipartition** means that all microstates are equally likely. Note that ergodicity and equipartition do not necessarily hold.

If $S = k_B \ln W$ then $S = 0$ means that $W = 1$ which means that there is only one arrangement. For example, if we are considering arrangements of electrons in an insulator then this corresponds to all fermion states below the Fermi temperature being occupied. If instead we are considering a Bose

condensate then this corresponds to all bosons being in the ground state. The third law states that at $T = 0$ we have $S = 0$ so $W = 1$ at $T = 0$, i.e. there is only one microstate, the ground state, at $T = 0$. This definition of entropy also shows that negative entropy is not possible as $W \geq 1$ so $\ln W \geq 0$. The fact that $S = k_B \ln W$ implies that all states are equally likely.

More generally the Gibbs entropy is defined as $S = -k_B \sum_i p_i \ln p_i$ where p_i is the probability of finding the system in microstate i . This definition of entropy is beyond the scope of this course however.

As an example of this statistical point of view consider a three particle system with two partitions, A and B . Let N_A be the number of particles in partition A and N_B be the number of particles in partition B . Then table 15.1 shows all possible microstates and number of macrostates. In general a system of N

Number of macrostates	Corresponding microstates
$W(N_A = 0) = 1$	(B, B, B)
$W(N_A = 1) = 3$	$(A, B, B), (B, A, B), (B, B, A)$
$W(N_A = 2) = 3$	$(A, A, B), (A, B, A), (B, A, A)$
$W(N_A = 3) = 1$	(A, A, A)

Table 15.1: The number of microstates and macrostates of a three particle, two part system.

particles the number of particles in A is

$$W(N_A = k) = \binom{N}{k} = \frac{N!}{k!(N-k)!}.$$

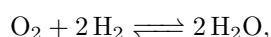
The ‘average’ state is far more likely, in this case the ‘average’ state has $N_A \approx N_B$. As $N \rightarrow \infty$ the peak width of a plot of $W(N_A = k)$ against k tends to $1/\sqrt{N}^{14}$. Here we have assumed that the three particles are distinguishable so that (A, B, B) is not the same microstate as (B, A, B) . If this is not the case then $W(N_A = 1) = W(N_A = 2) = 1$.

16 Phase Transitions

16.1 Gibbs Phase Rule

The number of independent variables which are needed to fully describe a thermodynamic equilibrium is $C + 2 - N_P$ where C is the number of chemical components (the number of chemical species minus constraints from reaction or charge balancing) and N_P is the number of phases. For example:

- Liquid water has $C = N_P = 1$ so needs $1 + 2 - 1 = 2$ independent variables. We usually choose P and T .
- An ice/water mix has $C = 1$ and $N_P = 2$ so needs $1 + 2 - 2 = 1$ variable. This can be seen as a result of an ice/water mix existing on the phase boundary, which is one-dimensional, so specifying T fixes P and vice versa.
- At the triple point of water we have $C = 1$ and $N_P = 3$ so we need $1 + 2 - 3 = 0$ variables. This can be seen as a consequence of the triple point being a unique point and therefore simply by stating ‘at the triple point’ we have already fixed all thermodynamic variables.
- A gaseous mixture of O_2 , H_2 , and H_2O has $C = 3$ and $N_P = 1$ so needs $3 + 2 - 1 = 4$ variables. We typically choose T and P as well as the amount of O_2 and the amount of H_2 , which we denote N_{O_2} and N_{H_2} respectively.
- If we consider the same mixture as above but now allow for a chemical reaction,



then $C = 3 - 1$ as we remove a chemical component by requiring this equation to balance, i.e. knowing the initial amounts of all species and also N_{O_2} and N_{H_2} at some later point we can find N_{H_2O} , the amount of H_2O .

¹⁴See the Statistics part of the Fourier analysis and statistics course, $k \sim \text{Binom}(p = 1/2, n = N) \rightarrow \text{Norm}(\mu = n/2, \sigma^2 = 1/N)$.

16.2 Ehrenfest's Order of Phase Transitions

At a phase boundary $g_1 = g_2$. Ehrenfest classified phase transitions by their **order** as follows:

1. First order phase transitions have the following properties:

- Discontinuous state variables, e.g. $s_1 \neq s_2$ and $v_1 \neq v_2$.
- Discontinuous first derivatives of free energy, e.g.

$$\left(\frac{\partial g_1}{\partial T}\right)_P \neq \left(\frac{\partial g_2}{\partial T}\right)_P.$$

2. Second order phase transitions have the following properties:

- Continuous state variables, e.g. $s_1 = s_2$ and $v_1 = v_2$.
- Discontinuous first derivatives of state variables, e.g.

$$\left(\frac{\partial s_1}{\partial T}\right)_P \neq \left(\frac{\partial s_2}{\partial T}\right)_P \implies c_{P,1} \neq c_{P,2},$$

$$\left(\frac{\partial v_1}{\partial T}\right)_P \neq \left(\frac{\partial v_2}{\partial T}\right)_P \implies \beta_1 \neq \beta_2,$$

and

$$\left(\frac{\partial v_1}{\partial P}\right)_T \neq \left(\frac{\partial v_2}{\partial P}\right)_T \implies K_1 \neq K_2.$$

- Continuous first derivatives of free energy, e.g.

$$\left(\frac{\partial g_1}{\partial T}\right)_P = \left(\frac{\partial g_2}{\partial T}\right)_P.$$

- Discontinuous second derivatives of free energy, e.g.

$$\left(\frac{\partial^2 g_1}{\partial T^2}\right)_P \neq \left(\frac{\partial^2 g_2}{\partial T^2}\right)_P.$$

3. Third order phase transitions have the following properties:

- Continuous state variables, e.g. $s_1 = s_2$ and $v_1 = v_2$.
- Continuous first derivatives of state variables, e.g.

$$\left(\frac{\partial s_1}{\partial T}\right)_P = \left(\frac{\partial s_2}{\partial T}\right)_P \implies c_{P,1} = c_{P,2},$$

$$\left(\frac{\partial v_1}{\partial T}\right)_P = \left(\frac{\partial v_2}{\partial T}\right)_P \implies \beta_1 = \beta_2,$$

and

$$\left(\frac{\partial v_1}{\partial P}\right)_T = \left(\frac{\partial v_2}{\partial P}\right)_T \implies K_1 = K_2.$$

- Discontinuous second order first derivatives of state variables, e.g.

$$\frac{\partial^2 s_1}{\partial T \partial P} \neq \frac{\partial^2 s_2}{\partial T \partial P}, \quad \text{and} \quad \frac{\partial c_{V,1}}{\partial V} \neq \frac{\partial c_{V,2}}{\partial V}.$$

- Continuous first and second order derivatives of free energy, e.g.

$$\left(\frac{\partial g_1}{\partial T}\right)_P = \left(\frac{\partial g_2}{\partial T}\right)_P, \quad \text{and} \quad \left(\frac{\partial^2 g_1}{\partial T^2}\right)_P = \left(\frac{\partial^2 g_2}{\partial T^2}\right)_P.$$

- Discontinuous third order derivatives of free energy, e.g.

$$\left(\frac{\partial^3 g_1}{\partial T^3}\right)_P \neq \left(\frac{\partial^3 g_2}{\partial T^3}\right)_P.$$

4. n th order phase transitions have the following properties:

- Continuous state variables with the first discontinuous derivative being the $(n-1)$ th derivative.
- Continuous derivatives of the free energy with the first discontinuous derivative being the n th derivative.

A first order transition is also called a discontinuous transition. Consider an isothermal process at first order phase boundary. Then

$$g_1 = g_2, \quad \left(\frac{\partial g_1}{\partial T}\right)_P \neq \left(\frac{\partial g_2}{\partial T}\right)_P, \quad \left(\frac{\partial g_1}{\partial P}\right)_T \neq \left(\frac{\partial g_2}{\partial P}\right)_T, \quad s_1 \neq s_2, \quad \text{and} \quad v_1 \neq v_2.$$

At a second order phase boundary

$$\left(\frac{\partial g_1}{\partial T}\right)_P = \left(\frac{\partial g_2}{\partial T}\right)_P, \quad \text{and} \quad \left(\frac{\partial g_1}{\partial P}\right)_T = \left(\frac{\partial g_2}{\partial P}\right)_T.$$

As well $s_1 = s_2$ so $\Delta s = 0$ meaning that the latent heat of this transition is $l = 0$, and $v_1 = v_2$ so $\Delta v = 0$. s and v are related by the Maxwell relation

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P.$$

Since $ds = dv = 0$ $dU = T ds - P dv = 0$ also. The Clausius–Clapeyron equation fails at second order (or higher) transitions as we have

$$\left(\frac{\partial P}{\partial T}\right)_{\text{pb}} = \frac{\Delta s}{\Delta v} = \frac{0}{0}.$$

There are two types of second order transitions:

1. **Critical fluctuations** – Regions of the system fluctuate into other phases in an uncorrelated way. For example parts of a paramagnet may align in some regions to act like a ferromagnet but on average there will still be no magnetisation unless an external field is applied, which means that this aligning is uncorrelated. Gradually these regions grow as the magnet is cooled to the Curie temperature and the regions start joining. The transitions then become correlated and the symmetry is broken and the magnetic moments align. This happens slowly enough that $\Delta s = 0$ and clearly $\Delta v = 0$.
2. **Coexistence** – A system consist of both phases at once and parts of the system move between the phases at a constant rate.

16.3 Clausius–Clapeyron Second Order Fix

Consider the entropy at two points, $A = (T, P)$ and $B = (T + dT, P + dP)$, on a phase boundary between two states, 1 and 2. Travelling along the phase boundary $\Delta S = 0$. Therefore

$$S_1(T, P) = S_2(T, P), \quad \text{and} \quad S_1(T + dT, P + dP) = S_2(T + dT, P + dP).$$

If we Taylor expand at B then we have

$$S_1(T, P) + \left(\frac{\partial S_1}{\partial T}\right)_P dT + \left(\frac{\partial S_1}{\partial P}\right)_T dP = S_2(T, P) + \left(\frac{\partial S_2}{\partial T}\right)_P dT + \left(\frac{\partial S_2}{\partial P}\right)_T dP.$$

Noting that the first terms on either sides are equal, $(\partial S/\partial T)_P = C_P/T$, and $(\partial S/\partial P)_T = -(\partial V/\partial T)_P = -V\beta$ then

$$\frac{C_{P,1}}{T} dT - V\beta_1 dP = \frac{C_{P,2}}{T} dT - V\beta_2 dP$$

which gives

$$\left(\frac{\partial P}{\partial T}\right)_{\text{pb}} = \frac{C_{P,1} - C_{P,2}}{TV(\beta_1 - \beta_2)} = \frac{c_{P,1} - c_{P,2}}{Tv(\beta_1 - \beta_2)}.$$

This is known as the first Ehrenfest equation. The second Ehrenfest equation can be derived in a similar way if we expand the volume at A and B instead of the entropy. The second Ehrenfest equation is

$$\left(\frac{\partial P}{\partial T}\right)_{\text{pb}} = \frac{\beta_2 - \beta_1}{\kappa_2 - \kappa_1}.$$

Hence the slope of the transition line relates $\Delta\beta$, $\Delta\kappa$, and ΔC_P .

In critical regions, $\pm\Delta T_{\text{crit}}$, around T_C the heat capacity is given by $C_V \propto (T - T_C)^{-\alpha}$ for some positive constant α . Thus $C_V \rightarrow \infty$ as $T \rightarrow T_C$. A similar correlation between magnetic spins has $\langle S_i, S_j \rangle \propto r^{-\nu} \rightarrow \infty$ as $r \rightarrow 0$. This power law dependence means that there is no characteristic scale for these quantities, i.e. they can become arbitrarily large. The universality conjecture is that α and ν are the same for all materials. From this we see that transitions can be characterised by large fluctuations.

16.4 Ising Ferro Magnet

The Ising model is a simple model of a magnetic transition. In this model near the Curie temperature

$$M \propto (T - T_C)^\beta$$

and

$$\chi = \frac{dM}{dB} \propto \left(\frac{c}{T - T_C}\right)^\gamma.$$

On a macroscopic scale we see $M \rightarrow 0$ as the magnet is heated from absolute zero to T_C . On a microscopic we see neatly aligned spins lose their alignment as thermal effects start to dominate. Near the Curie temperature χ becomes infinite, another example of large fluctuations at a transition.

16.5 Metastability

The equation of state for a single phase of a material is a surface in (P, V, T) -space. The equation of state for a second phase is a different surface in (P, V, T) -space. The equation of state for the material is then a combination of the equations of state for each phase choosing whichever has the lowest Gibbs free energy at any given point. The material can thus jump discontinuously from one phase to another. It is common for a material to have properties that would put it in one phase but to not yet have made the transition, while in the original phase but with properties that should be in the second phase we say that the material is in a **metastable** phase. For example water can be cooled below 0°C without freezing, called **supercooled** water. As soon as the water begins to freeze it will all quickly solidify. Similarly water can be heated to above 100°C without boiling, called **superheated** water. As soon as the water begins to boil it will all quickly vaporise.

16.6 Liquid Helium

Liquid helium has two phases. When cooled down from a gas the helium first condenses to the phase HeI which acts like a normal fluid. When cooled further since ^4He is bosonic (spin 0) it can form a Bose condensate where all ^4He atoms are in the same, zero-entropy, state, called a **superfluid**. This is called HeII, it has bizarre properties such as no viscosity. In reality the transition to HeII doesn't happen until the helium is cooled below $T_\lambda = 2.2\text{K}$ ¹⁵ and not all helium is ^4He meaning that we end up with coexisting HeI and HeII. The viscosity, η , of this combination is the harmonic average, $\eta^{-1} = \eta_{\text{HeI}}^{-1} + \eta_{\text{HeII}}^{-1}$.

16.7 Superconductivity

Many materials when cooled below a certain critical temperature, T_c , have no resistance as electrons pair up forming bosons, called Cooper pairs, which can move unimpeded through the material. For example pure indium, In, is a superconductor below $T_c = 3.4\text{K}$. This is a coexistence type phase transition as electrons slowly pair up.

¹⁵ λ is used to denote the point at which HeI transitions to HeII because the phase diagram at this point looks a bit like a λ .

17 Chemical Potential

Up until now we have considered almost exclusively closed systems. In these systems the number of particles is fixed and therefore we ignore it. In an open system the number of particles is not fixed. To take this into account we modify the central equation:

$$dU = T dS - P dV + \mu dN, \quad \text{where} \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}.$$

Here N is the number of particles and μ is the **chemical potential**. We can view μdN as another form of work. This is not a particularly useful definition as it is difficult to change the number of particles without also changing the entropy. It is more convenient to consider the other chemical potentials. They have the same definitions,

$$F = U - TS, \quad H = U + PV, \quad \text{and} \quad G = H - TS = F + PV,$$

but now in differential form they have an extra term:

$$\begin{aligned} dF &= dU - T dS + S dT \\ &= T dS - P dV + \mu dN - T dS - S dT \\ &= \mu dN - P dV - S dT, \\ dH &= dU + P dV + V dP \\ &= T dS - P dV + \mu dN + P dV + V dP \\ &= \mu dN + T dS + V dP, \end{aligned}$$

and

$$\begin{aligned} dG &= dH - T dS - S dT \\ &= T dS - P dV + \mu dN - T dS - S dT \\ &= \mu dN + V dP - S dT. \end{aligned}$$

This gives alternative definitions of μ :

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

If there are multiple chemical species present then we assign each a different number, N_i , and potential, μ_i , and in the above equations make the replacement

$$\mu dN \rightarrow \sum_i \mu_i dN_i.$$

Suppose we have a system with N particles and we change the system to have αN particles. Then all extensive quantities (quantities that depend on the amount of matter) increase by a factor of α . Importantly this is true for the Gibbs free energy, i.e. the Gibbs free energy of αN particles is α times the Gibbs free energy of N particles, or as an equation

$$\alpha G(P, T, N) = G(P, T, \alpha N).$$

Differentiating both sides with respect to α we then have

$$\begin{aligned} G(P, T, N) &= \left(\frac{\partial G(P, T, \alpha N)}{\partial \alpha} \right)_{P,T} \\ &= \left(\frac{\partial G(P, T, \alpha N)}{\partial (\alpha N)} \right)_{P,T} \left(\frac{\partial (\alpha N)}{\partial \alpha} \right)_{P,T} \\ &= N \left(\frac{\partial G(P, T, \alpha N)}{\partial (\alpha N)} \right)_{P,T} \\ &= N \left(\frac{\partial G(P, T, \alpha N)}{\partial N} \right)_{P,T} \left(\frac{\partial N}{\partial \alpha N} \right)_{P,T} \end{aligned}$$

$$\begin{aligned}
&= N \left(\frac{\partial G(P, T, \alpha N)}{\partial N} \right)_{P, T} \left[\left(\frac{\partial \alpha N}{\partial N} \right)_{P, T} \right]^{-1} \\
&= \frac{N}{\alpha} \left(\frac{\partial G(P, T, \alpha N)}{\partial N} \right)_{P, T} \\
&= \frac{N}{\alpha} \left(\frac{\partial \alpha G(P, T, N)}{\partial N} \right)_{P, T} \\
&= N \left(\frac{\partial G(P, T, N)}{\partial N} \right)_{P, T} \\
&= N\mu.
\end{aligned}$$

So for a pure substance $G = \mu N$. The chemical potential is then $\mu = G/N$. Hence

$$d\mu = \frac{1}{N} dG + G d\frac{1}{N}$$

It can be shown then that

$$d\mu = -s dT + v dP.$$

So we can, for a pure substance, write the chemical potential as a function of P and T only. Also

$$s = - \left(\frac{\partial \mu}{\partial T} \right)_{P, N}, \quad \text{and} \quad v = \left(\frac{\partial \mu}{\partial P} \right)_{T, N}.$$

17.1 Equilibration of Two Part System

Consider a closed system divided into two parts, A and B . The two parts are separated by a freely moving permeable membrane (i.e. the volume is not constant and particles can move between the sides). Since the whole system is isolated total quantities are preserved such as the internal energy, matter, and volume. This means that

$$dU_A + dU_B = 0, \quad dN_A + dN_B = 0, \quad \text{and} \quad dV_A + dV_B = 0.$$

By the second law we know that

$$dS_A + dS_B \geq 0.$$

From the central equation we have

$$dS(U, V, N) = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN.$$

Splitting each change into the change in the two separate parts and using the fact that the change in A is equal and opposite to the change in B , e.g. $dU_A = -dU_B$, we have

$$\left(\frac{1}{T_A} - \frac{1}{T_B} \right) dU_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B} \right) dV_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B} \right) dN_A = dS \geq 0.$$

At equilibrium we will have $T_A = T_B$, $P_A = P_B$, and $\mu_A = \mu_B$. We can then interpret this equation as the three changes that can happen to bring the system into equilibrium:

- The first term corresponds to energy flowing from the hotter section to the cooler section until $T_A = T_B$, i.e. thermal equilibrium.
- The second term corresponds to volume moving from the higher pressure to the lower pressure until $P_A = P_B$, i.e. mechanical equilibrium.
- The third term corresponds to particles flowing from a high chemical potential to a low chemical potential until $\mu_A = \mu_B$, i.e. chemical equilibrium.

We see that particles (mass) flow along gradients of chemical potential. We can use this as an alternative view of gravity. For example planets are made of many layers. The formation of these layers can be seen as a result of a chemical potential

$$\mu = u - Ts + Pv + mgh$$

where the last term corresponds to gravity and causes a position close to the centre to be more favourable and how favourable depends on the mass of the particle.

An important assumption that we have made here is that non-interacting species in the same system can be treated as independent ideal gases. This can be viewed as a consequence of two laws:

- Dalton's law – The total pressure, P , is equal to the sum of the partial pressures, p_i . The partial pressure of a species is the pressure that would occur if that were the only species present in that volume and at the same temperature.
- Raoult's law – Partial pressure is proportional to the concentration meaning

$$p_i V = N_i R T.$$

For example we can consider air (ignoring minor constituents) as two ideal gasses. One N_2 gas and one O_2 gas with $N_{N_2} \approx 4N_{O_2}$ as there is about four times as much N_2 in the air as there is O_2 . This is the same as how we considered photons in a cavity as an infinite number of different systems, one for each wavelength.

17.2 Solubility

Suppose we are dissolving a gas, x , in water. We wish to know the concentration, c_x , of this gas at equilibrium. We do this in an open system with boundary conditions that temperature and pressure are both constant at T_0 and P_0 respectively as well as a constant chemical potential for x , $\mu_x^{(0)}$ which we can achieve by having a constant partial pressure, p_x , for the gas above the water. Suppose that the specific enthalpy of solution (i.e. the enthalpy released upon dissolving one mole of x) is δh_x .

By Raoult's law

$$p_x = P_0 \frac{N_x}{N} = P_0 c_x.$$

Then

$$\mu_x^{(0)} = \mu_x = h - T_0 s = \delta h + R T_0 \ln \frac{p_x}{P_0}$$

using the fact that the entropy of a real gas is

$$s = -R \ln \frac{p_x}{P_0}.$$

Rearranging this we have

$$c_x = \exp \left(\frac{\mu_x^{(0)} - \delta h}{R T_0} \right).$$

If x is insoluble in water then $\delta h \gg \mu_x^{(0)}$, however we still have a non-zero concentration of x in the water. If x is soluble in water then $\delta h < \mu_x^{(0)}$. This causes problems because the concentration will then be greater than one. This is because the ideal gas assumption is not valid for a soluble gas as there is interaction between the gas and the water.

17.3 Thermodynamics in Chemistry

This section is non-examinable

In chemistry molecules can react to form other molecules. We can assign a chemical potential for each species. For a multiple species system the Gibbs free energy is

$$dG = -S dT + V dP + \sum_i \mu_i dN_i.$$

The total Gibbs free energy is also given by

$$G = \sum_i \mu_i N_i \implies dG = \sum_i (N_i d\mu_i + \mu_i dN_i).$$

Combining these two equations for dG we have

$$\sum_i N_i d\mu_i = -S dT + V dP.$$

This is known as the Gibbs–Duhem relation. It gives the balance of the concentration of each component.

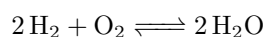
For a closed system with fixed P and T we have $dP = dT = 0$. Reactions will occur to minimise the Gibbs free energy which in the case of $dP = dT = 0$ means that at equilibrium

$$dG = \sum_i \mu_i dN_i = 0.$$

The concentrations, N_i , are internal degrees of freedom which we can change to minimise G even if external degrees of freedom are fixed. The values of dN_i are constrained by the reaction equation. If b_i moles of i appear in the left hand side of the reaction equation or $-b_i$ moles of i appear in the right hand side of the reaction equation then conservation of matter means that

$$\sum b_i dN_i = 0.$$

For example consider the reaction



here $b_{\text{H}_2} = 2$, $b_{\text{O}_2} = 1$, and $b_{\text{H}_2\text{O}} = -2$ (negative as H_2O appears on the right hand side) meaning that

$$2 dN_{\text{H}_2} + dN_{\text{O}_2} - 2 dN_{\text{H}_2\text{O}} = 0.$$

Combining this with minimising G and we have at equilibrium that

$$\sum_i b_i \mu_i = 0.$$

For our example

$$2\mu_{\text{H}_2} + \mu_{\text{O}_2} - \mu_{\text{H}_2\text{O}} = 0.$$

So at chemical equilibrium the total chemical potential of the reagents is equal to the total chemical potential of the products. Typically we start with more reactants and we react them until equilibrium is achieved.

For an ideal gas with N held constant we have

$$\begin{aligned} d\mu &= \frac{1}{N} dG \\ &= dg \\ &= \left(\frac{\partial(G/N)}{\partial T} \right)_{P,N} dT + \left(\frac{\partial(G/N)}{\partial P} \right)_{T,N} dP \\ &= \frac{S}{N} dT + \frac{V}{N} dP \\ &= c_P dT + \frac{RT}{P} dP. \end{aligned}$$

Integrating over $[0, T]$ and $[P_0, P]$ we get

$$\mu = c_P T + RT \ln \frac{P}{P_0}.$$

Notice that μ is dependent on $P \propto N$ so increasing N at a fixed pressure and temperature will increase μ .

A dilute solution can be approximated as a mixture of ideal gases. For this reason it is called an ideal solution. The pressure of the entire solution is then

$$P = \sum_i p_i$$

and for each individual component

$$p_i V = N_i R T.$$

The Gibbs free energy is then

$$dG = V \sum_i dp_i - S dT + \sum_i \mu_i dN_i.$$

For an isothermal reaction, $dT = 0$, we have

$$dG = \sum_i d\mu_i = \sum_i \frac{RT}{p_i} dp_i.$$

Integrating over $[0, \mu_i^{(0)}]$ we get

$$\mu_i = \mu_i^{(0)} + RT \ln \frac{p_i}{p_i^{(0)}}$$

where $\mu_i^{(0)}$ is the chemical potential of species i at reference pressure $p_i^{(0)}$ and p_i is the partial pressure of species i . Hence

$$\sum_i b_i \left[\mu_i^{(0)} + RT \ln \frac{p_i}{p_i^{(0)}} \right] = 0$$

A bit of rearranging gives

$$\ln K = \ln \left[\prod_i \left(\frac{p_i}{p_i^{(0)}} \right)^{b_i} \right] = -\frac{1}{RT} \sum_i b_i \mu_i^{(0)}$$

so

$$K = \prod_i \left(\frac{p_i}{p_i^{(0)}} \right)^{b_i} = \exp \left[-\frac{1}{RT} \sum_i b_i \mu_i^{(0)} \right].$$

This is the definition of the equilibrium constant¹⁶, K .

At low temperatures (low when comparing $k_B T$ to the chemical energy)

- TS is negligible and μ is the enthalpy.
- $\sum_i b_i \mu_i$ is then the enthalpy of reaction.
- $K(T)$ looks like the Boltzmann factor, $\exp(-\Delta E/k_B T)$.

We can measure μ_i n times (once for each species present) rather than measuring K $n!$ times (once for every possible reaction of n species). Clearly this is much easier.

18 Applications of the Chemical Potential

For a system of multiple chemical species the chemical potential of the i th species is

$$\mu(T, p_i) = g(T, p_i) = g_0 + RT \ln \frac{p_i}{P_0}.$$

Here g_0 is the Gibbs free energy at some reference pressure P_0 . We usually choose P_0 to be the total pressure as then $p_i/P_0 = x_i$ is the fraction of species i in the mix, which is one way of measuring the concentration.

The specific entropy of the i th species is then

$$s_i = - \left(\frac{\partial g}{\partial T} \right)_P = R \ln x_i.$$

¹⁶Not really a constant, it depends on T

The total entropy is then the sum of the entropies weighted by the prevalence of the relevant species¹⁷:

$$S = - \sum_i x_i s_i = \sum_i x_i R \ln x_i.$$

This assumes no interactions but is still relatively accurate if there are interactions.

Consider a two component system with substances A and B . The enthalpy is

$$H = H_0 x_A x_B$$

where H_0 is some constant characterising the strength of interactions between the substances. Notice that if x_A or x_B are zero then there is no enthalpy as we don't really have a mixture if the concentration of one component is zero. The enthalpy is maximised when $x_A = x_B = 1/2$, note that $\sum_i x_i = 1$ from the definition of x_i . The Gibbs free energy of this system is

$$G = H_0 x_A x_B + x_A RT \ln x_A + x_B RT \ln x_B = H_0 x_A (1 - x_A) + x_A RT \ln x_A + (1 - x_A) RT \ln x_A.$$

Then

$$\left(\frac{\partial G}{\partial x_A} \right)_T = \frac{H_0}{RT} (1 - 2x_A) + \ln \frac{x_A}{1 - x_A}.$$

We seek to minimise Gibbs free energy. For this reason we look for extrema of G . We find that $(\partial G / \partial x_A)_T = 0$ at $x_A = 1/2$. This is a minimum if H_0 is small or a maximum if H_0 is large. In the case that H_0 is large there are two other minima in the interval $[0, 1]$. If this is the case then the system minimises the free energy by separating into two phases. The phase at the first minima corresponds to a mixture that is mostly substance B and the phase at the second minima corresponds to a mixture that is mostly substance A . These are still mixtures of both substances unless the minima occur at $x_A = 0, 1$ which doesn't happen. One example of a mixture that does this is oil and water. We use a convex hull, which is simply a tangent line between the minima, to show the Gibbs free energy when it is minimised. This is shown in figure 18.1.

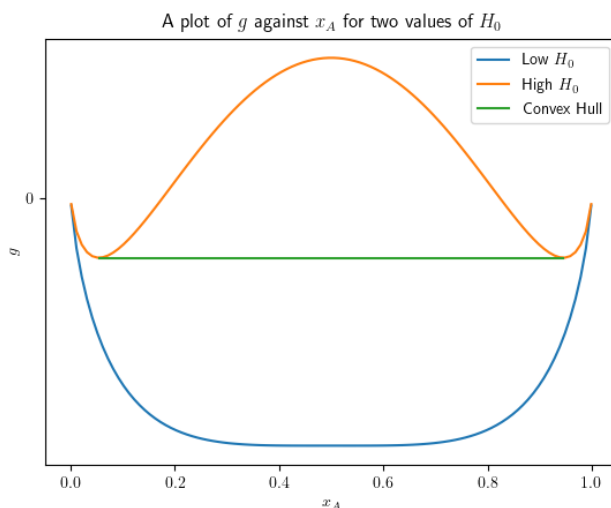


Figure 18.1: The Gibbs free energy of a two substance mixture. x_A is the concentration fraction of substance A . Plotted for two different values of H_0 to show the two possible shapes.

At high temperatures the entropy dominates and the system tends towards being an ideal solution, starting out of equilibrium and moving towards an even mix of A and B . The difference in chemical potentials is what causes this motion.

¹⁷Sometimes this is given as $-\sum_i k_B p_i \ln p_i$ where p_i is the probability of being in the i th state, which in this case is the same as the ratio of that state to the total number of states.

How a mixture separates at a given concentration depends on the curvature of the Gibbs free energy at that concentration. If the curvature is negative,

$$\left(\frac{\partial^2 g}{\partial x_A^2}\right)_T < 0,$$

for example at the maximum of a curve, then separating is spontaneous (i.e. decreases the total Gibbs free energy). This is because a splitting the mixture in two and moving part to a lower value of x_A and part to a higher value of x_A reduces the net Gibbs free energy. On the other hand if the curvature is positive,

$$\left(\frac{\partial^2 g}{\partial x_A^2}\right)_T > 0,$$

then the same split that decreased the net Gibbs free energy for negative curvature will increase the average Gibbs free energy. Suppose, for example, that the mixture is at a concentration that puts it just slightly past the first minimum with a high value of H_0 . The curvature here is positive. The only way for the mixture to separate without increasing the Gibbs free energy is to do it in such a large step that one part of the mixture moves past the maximum and over to the other side. This is unlikely to happen so takes a while. For this reason the mixture is metastable at this concentration as it will eventually separate but it will take a long time.

The section of the graph with negative curvature is called spinodal and the section with positive curvature is called binodal.

18.1 Chemical Potential Doing Weird Things

The second law says that entropy must increase and that this can happen by moving towards lower chemical potentials. However the second law doesn't say how this is to happen and there are some scenarios where something weird happens.

18.1.1 Ammonia Fountain

Ammonia, NH_3 , is very soluble in water. Consider the setup in figure 18.2.

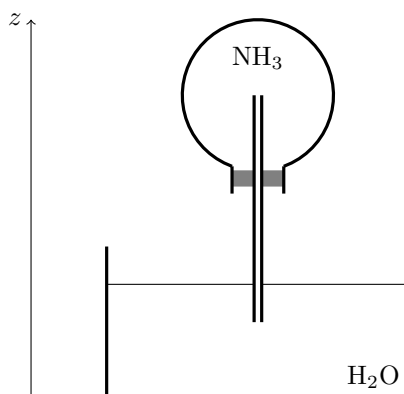


Figure 18.2: The setup for an ammonia fountain.

This is called an ammonia fountain because the ammonia dissolves in the water so well that the decrease in Gibbs free energy from this occurring is greater than the increase in Gibbs free energy it would take to move the water to the top flask so the water shoots up the pipe and comes out into the top flask like a fountain. The change in Gibbs free energy at constant pressure and temperature is

$$dg = dh - \underbrace{s dT + v dP}_{=0} + mg dz$$

so as long as $dh < mg dz$ the Gibbs free energy will still decrease when the water moves upwards. This same effect will work with any gas and liquid as long as the gas is soluble enough that this inequality holds.

18.1.2 Liquid Helium Fountain

The liquid helium fountain is a similar effect to the ammonia fountain. The setup is shown in figure 18.3. A bath of He II, which is a mixture of He and superfluid He contains a capsule which has a porous plug

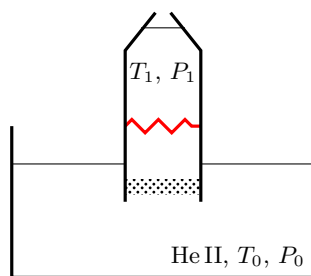


Figure 18.3: The setup for a liquid helium fountain.

that allows only superfluid He through. The superfluid He in the capsule is then heated up shoots out the top of the capsule in a fountain. It then falls back down into the bath. This process can go on indefinitely as long as we keep supplying heat to the helium. Since the superfluid components are in contact through the porous plug they must have the same chemical potential in both the bath and the capsule. That is $\Delta\mu = 0$. Since we are heating the gas $\Delta T \neq 0$ and since $\Delta\mu = v\Delta P - s\Delta T$ we must have an increase in pressure that counteracts the increase in T , it is this pressure that causes the helium to shoot out into the atmosphere which is at $P_0 < P_1$.

18.2 Osmosis

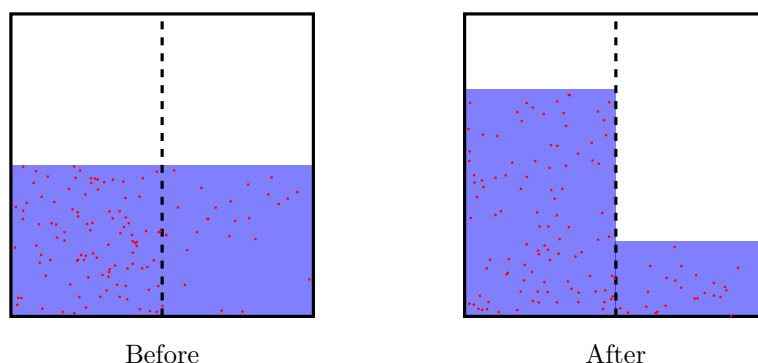


Figure 18.4: Osmosis – The spontaneous transport of water across a semi-permeable membrane to a region of higher solute concentration.

Osmosis is the spontaneous transport of water across a semi-permeable membrane to a region of higher solute concentration. Consider the setup in figure 18.4. Here water is placed in a container and divided in two sections, A on the left and B on the right, by a semi-permeable membrane which will allow through water and nothing else. Sugar is dissolved in the water to a high concentration on the left and a lower concentration on the right. The water will, given time, move to the left even though this increases the pressure on this side.

Since the water is in contact with itself the chemical potential of the water in A must be the same as the chemical potential of the water in B , $\mu_A^W = \mu_B^W$. However the sugar does not have the same chemical potential on both sides, $\mu_A^S \neq \mu_B^S$. The sugar cannot move across the membrane to correct this, but the water can, so it does.

In the simplest case the molecules don't interact with each other and so the chemical potentials are proportional to the pressure as this is the only thing causing change. That is $\mu^W \propto p^W$ and $p_A^W = p_B^W$. The total pressure is $P = \sum_i p_i$ and the total pressure in A will be higher than the total pressure in B by p_B^S .

In a less simple case the molecules can interact and μ^W depends on the sugar concentration. If the sugar and water attract each other (which they do as sugar is soluble in water) then, considering the difference

between terms on left and right, we have $\Delta\mu^W < 0$ so to have $\Delta g^W = 0$ we need $\Delta p^W > 0$.

18.3 Electrons

A metal in its ground state will have all electrons occupying states up to the Fermi energy, E_F . If two metals with different Fermi energies are placed in electrical contact then electrons will flow from the metal with the higher Fermi energy to the metal with the lower Fermi energy until the two equilibrate. The voltage this creates will be

$$V = \frac{W_1 - W_2}{e}$$

where e is the charge of an electron and W_i is the work done to move an electron from infinity ($E = 0$) to the metal ($E = E_F$) for metal i .

18.4 Hurricanes

Hurricanes behave much like a heat engine. The ocean is the hot reservoir ($T \approx 300$ K) and the top of the atmosphere is the cold reservoir ($T \approx 200$ K). The work done is used creating wind. The cycle approximates the Carnot cycle:

- Isothermal expansion – Air spirals towards the eye of the storm and absorbs water.
- Adiabatic expansion – Hot air rises to a lower pressure.
- Isothermal compression – Water vapour condenses and falls as rain releasing latent heat.
- Adiabatic compression – In theory the air drops back to sea level, in practice the air simply leaves the system like an exhaust.

The initial spinning is caused by the Coriolis force causing the air to spin a little and then the heat engine is self perpetuating causing more and more spinning.

18.5 Thermoelectric Material

A thermoelectric material is one where the chemical potential of the electrons, μ_e , depends on the temperature. If a temperature gradient is applied then the electrons will flow either along the gradient or against it (holes flowing along it) depending on the nature of the material. This can be used to make a thermoelectric heat engine. Two thermoelectric materials with opposite behaviour are placed between a hot and cold heat reservoir. One end of the materials is placed in electrical contact and the other ends are connected by a circuit. The thermoelectric material in which the electrons flow with the temperature gradient will push materials from the hot end to the cold end. From here they can flow round the circuit into the cold end of the other thermoelectric material which will push the electrons from the cold end to the hot end where they are added back onto the first thermoelectric material for the whole process to start again.

Part II

Statistical Mechanics

19 Why Statistical Mechanics?

Thermodynamics was developed phenomenologically. This means that observations were made and maths was found to fit them and then tested against new scenarios. This is useful if the only thing we care about is getting the answer at the end but it is limited to scenarios that are similar to ones we have already seen and doesn't actually tell us anything about *why* something happens. Thermodynamics is a macroscopic approach, we have macroscopic quantities, like pressure, volume, and temperature, and we study how these change.

In theory we can take a microscopic approach where we start with information such as the position and momentum of all particles and then perform some sort of calculation which will tell us the same

information at a later time. That calculation may be classical or quantum but in general is not that difficult for an individual molecule. The problem is we don't have individual molecules, we have a very large number of molecules which are all interacting. This causes two problems with the deterministic approach.

First even for a small amount of material we have a huge amount of data. For a single mole of gas ignoring interactions between molecules we have 6 degrees of freedom. One for each possible direction to get the position and one for each possible direction to get the momentum. If we include interactions this will just increase the number of degrees of freedom. So for a mole of gas we have at least $6N_A \approx 1.2 \times 10^{24}$ degrees of freedom. Suppose this was stored as 8 bit numbers. We would need $6N_A/8 \approx 4.5 \times 10^{23}$ B = 4.5×10^6 PB = 450 ZB. For Google stores about 1×10^{18} B to 1.5×10^{18} B or 10 EB to 15 EB of data. So we would need approximately 30000 Googles worth of data. This sort of data storage capacity simply does not exist. All of this is just to *store* the bare minimum amount of data. If we want to start performing calculations then the amount of computing power and time that we need would also be completely infeasible.

The second problem is that in general most systems of interest are modelled by systems of differential equations. For each degree of freedom of this system we need an initial value. This value will have to be the result of a measurement and as such will have some amount of error. A non-linear system of differential equations with more than two degrees of freedom is chaotic in that a small change to the initial conditions will create a large change in the output. For example if one degree of freedom of the system is a which has initial value $a(t=0) = a_0 \pm \delta a$ then if we consider the solution with initial conditions a_0 and $a_0 + \delta a$ then at time t the average separation between these results will be $e^{\lambda t} \delta a$. Here λ , known as the Lyapunov exponent, is a characteristic of the system and measures how fast solutions diverge. After $t \approx \lambda$ the model will have almost no predictive power as the possible solutions cover such a wide range. For example in the UK the weather is a chaotic system and $\lambda \approx 3$ days. This means that after 3 days weather prediction is almost pointless.

The result of this is that even if we did have the computing power and the ability to measure with the bare minimum quantum uncertainty we still wouldn't be able to make long term predictions. For this reason the deterministic approach is simply not possible. Instead we use statistical mechanics where we consider microscopic properties and then use statistical techniques to make predictions about macroscopic properties based on these properties. For example we measure the velocity of particles, fit them to a Maxwell-Boltzmann distribution, and then use this to predict the temperature.

20 Probability Part One

20.1 What is Probability

There are two main views on what exactly we mean by the probability of an event. The first is the frequentist view where if we perform N trials and observe an event n times out of those N trials then we say the probability of that event is

$$P = \lim_{N \rightarrow \infty} \frac{n}{N}.$$

The second view is the degree of belief we have that a certain event will occur. For example if there are q possible events and we believe they are all equally likely then the probability of any one particular event is $1/q$. Fortunately both views can be made to give the same numbers and follow the same rules.

20.2 Probability Rules

A random variable is one which can take on a different value every time we measure it. A random variable can be continuous or discontinuous. Typically the only difference is that a sum becomes an integral or vice versa. In this section we will take X as a discrete random variable which can take values $\{X_i\}$ and has probability distribution P meaning that the probability that measuring X gives the result X_i is $P(X_i)$. We will take x as a continuous random variable with probability density function (PDF) p meaning that the probability of measuring x to be in $[x, x + dx]$ is $p(x) dx$.

One of the most important things about a probability distribution or PDF is that it is normalised. This

means that

$$\sum_i P(X_i) = 1, \quad \text{or} \quad \int p(x) dx = 1$$

where the sum is over all possible values of i and the integral is over all possible values of x .

If X_1 and X_2 are mutually exclusive events, that is both cannot occur at once, then the probability of X_1 or X_2 is

$$P(X_1 \text{ or } X_2) = P(X_1 \vee X_2) = P(X_1 \cup X_2) = P(X_1) + P(X_2).$$

If X_1 and X_2 are independent events, that is the value of X_1 has no effect on the value of X_2 then the probability of X_1 and X_2 is

$$P(X_1 \text{ and } X_2) = P(X_1 \wedge X_2) = P(X_1 \cap X_2) = P(X_1)P(X_2).$$

The average value of X/x is defined by

$$\bar{X} = \sum_i X_i P(X_i), \quad \text{or} \quad \bar{x} = \int xp(x) dx.$$

The variance of X/x is defined by

$$\text{Var}(X) = \overline{\Delta X^2} = \overline{(X - \bar{X})^2} = \overline{X^2} - \bar{X}^2, \quad \text{or} \quad \text{Var}(x) = \overline{\Delta x^2} = \overline{(x - \bar{x})^2} = \overline{x^2} - \bar{x}^2.$$

The mean of a function, f , is

$$\overline{f(X)} = \sum_i P(X_i) f(X_i), \quad \text{or} \quad \overline{f(x)} = \int p(x) f(x) dx.$$

20.3 Binomial Distribution

20.3.1 Counting

The way of selecting n distinguishable items from N items is

$$N(N-1)(N-2)\cdots(N-n+2)(N-n+1) = \frac{N!}{(N-n)!}.$$

This is because there are N options for the first item, $N-1$ for the second and so on down to $N-n+1$ options for the final times. This takes into account the ordering of the items, this is most obvious when we consider the number of ways of selecting N items from N items which gives

$$\frac{N!}{(N-N)!} = N!.$$

We know that $N!$ is the number of ways of arranging N items. If we don't care about order, possibly because the items are indistinguishable, then we correct for over-counting by dividing by the number of arrangements of the n items we selected, that is dividing by $n!$. Thus the way of selecting n items from N indistinguishable items is

$$\binom{N}{n} = \frac{N!}{n!(N-n)!}.$$

Coincidentally this is the same binomial coefficient that appears in

$$(a+b)^N = \sum_{n=0}^N \binom{N}{n} a^n b^{N-n}.$$

20.3.2 Binomial Distribution

The binomial distribution is the probability distribution for the number of successes out of N trials if the probability of success on any one trial is p . The distribution is

$$P(n) = \binom{N}{n} p^n (1-p)^{N-n}.$$

The first term accounts for the number of ways that we can get n successes out of N trials. The second term, p^n accounts for the probability of getting n successes and the final term, $(1-p)^{N-n}$, accounts for the probability that the rest of the trials are failures.

As a probability distribution it is important that this is normalised. This is fairly easy to see if we use the binomial coefficient's original definition.

$$\sum_{n=0}^N P(n) = \sum_{n=0}^N \binom{N}{n} p^n (1-p)^{N-n} = (p + (1-p))^N = 1^N = 1.$$

First consider

$$\begin{aligned} \left. \frac{\partial}{\partial \alpha} \sum_{n=0}^N \binom{N}{n} (\alpha p)^n (1-p)^{N-n} \right|_{\alpha=1} &= \left. \sum_{n=0}^N \binom{N}{n} n \alpha^{n-1} p^n (1-p)^{N-n} \right|_{\alpha=1} \\ &= \sum_{n=0}^N \binom{N}{n} n p^n (1-p)^{N-n} \\ &= \sum_{n=0}^N n P(n) \\ &= \bar{n}. \end{aligned}$$

If we then start from the same place and proceed slightly differently we get

$$\begin{aligned} \left. \frac{\partial}{\partial \alpha} \sum_{n=0}^N \binom{N}{n} (\alpha p)^n (1-p)^{N-n} \right|_{\alpha=1} &= \left. \frac{\partial}{\partial \alpha} (\alpha p + (1-p))^N \right|_{\alpha=1} \\ &= pN (\alpha p + (1-p))^{N-1} \Big|_{\alpha=1} \\ &= pN (p + (1-p))^{N-1} \\ &= pN \end{aligned}$$

Hence

$$\bar{n} = pN.$$

We can calculate the variance in a similar way. We start with

$$\begin{aligned} \left. \frac{\partial}{\partial \alpha} \frac{\partial}{\partial \beta} \sum_{n=0}^N \binom{N}{n} (\alpha \beta p)^n (1-p)^{N-n} \right|_{\alpha=\beta=1} &= \left. \frac{\partial}{\partial \alpha} \sum_{n=0}^N \binom{N}{n} n \beta^{n-1} (\alpha p)^n (1-p)^{N-n} \right|_{\alpha=\beta=1} \\ &= \left. \sum_{n=0}^N \binom{N}{n} n^2 \alpha^{n-1} \beta^{n-1} p^n (1-p)^{N-n} \right|_{\alpha=\beta=1} \\ &= \sum_{n=0}^N \binom{N}{n} n^2 p^n (1-p)^{N-n} \\ &= \sum_{n=0}^N n^2 P(n) \\ &= \overline{n^2}. \end{aligned}$$

Then from the same starting point preceding slightly differently we have

$$\begin{aligned}
\frac{\partial}{\partial \alpha} \frac{\partial}{\partial \beta} \sum_{n=0}^N \binom{N}{n} (\alpha \beta p)^n (1-p)^{N-n} \Big|_{\alpha=\beta=1} &= \frac{\partial}{\partial \alpha} \frac{\partial}{\partial \beta} (\alpha \beta p + (1-p))^N \Big|_{\alpha=\beta=1} \\
&= \frac{\partial}{\partial \alpha} \alpha p N (\alpha \beta p + (1-p))^{N-1} \Big|_{\alpha=\beta=1} \\
&= p N (\alpha \beta p + (1-p))^{N-1} \Big|_{\alpha=\beta=1} \\
&\quad + \alpha \beta p^2 N (N-1) (\alpha \beta p + (1-p))^{N-2} \Big|_{\alpha=\beta=1} \\
&= p N (p + (1-p))^{N-1} + p^2 N (N-1) (p + (1-p))^{N-2} \\
&= p N + p^2 N (N-1) \\
&= p N + p^2 N^2 - p^2 N
\end{aligned}$$

So

$$\overline{n^2} = pN + p^2 N^2 - p^2 N.$$

Thus

$$\text{Var}(n) = \overline{\Delta n^2} = \overline{n^2} - \bar{n}^2 = pN + p^2 N^2 - p^2 N - p^2 N^2 = pN - p^2 N = Np(1-p).$$

To compare the mean and variance we use the standard deviation, which is the square root of the variance, and we see that

$$\frac{\sqrt{\Delta n^2}}{\bar{n}} = \frac{\sqrt{Np(1-p)}}{Np} = \frac{\sqrt{1-p}}{\sqrt{Np}} \sim \frac{1}{\sqrt{N}}$$

so we see as N increases we expect the width of the distribution to decrease as $N^{-1/2}$.

20.4 Stirling Approximation

We will often need the factorial of very large numbers, on the order of $N_A = 6.02 \times 10^{23}$. These values simply cannot be computed due to the size of the numbers and the number of operations required. We can however approximate them very well. One of the most common approximations for factorials is **Stirling's approximation**. For large N

$$\ln(N!) \approx N \ln N - N \iff N! + \mathcal{O}(\ln N) \approx e^{N \ln N - N} = e^{\ln N^N} e^{-N} = N^N e^{-N}.$$

Notice that N^N is huge and e^{-N} decays (relatively) slowly so for large N this will be a very large number. We can actually be even more accurate if we say that

$$\ln(N!) \approx N \ln N - N + \frac{1}{2} \ln(2\pi N) + \mathcal{O}(1/N) \iff N! \approx \sqrt{2\pi N} \left(\frac{N}{e}\right)^N.$$

We often don't need this level of accuracy or the added complexity.

We will now justify this approximation more than 'well $N!$ is really big and so is N^N '. We start by considering

$$\begin{aligned}
\ln(N!) - \frac{1}{2} \ln 1 + \frac{1}{2} \ln N &= \ln(1 \cdot 2 \cdots (N-1)N) - \frac{1}{2} \ln 1 - \frac{1}{2} \ln N \\
&= \ln 1 + \ln 2 + \cdots + \ln(N-1) + \ln N - \frac{1}{2} \ln 1 - \frac{1}{2} \ln N \\
&= \frac{1}{2} \ln 1 + \ln 2 + \cdots + \ln(N-1) + \frac{1}{2} \ln N.
\end{aligned}$$

We now compare this with the trapezium rule for approximating an integral as a series of rectangles and we see that

$$\ln(N!) - \frac{1}{2} \ln 1 - \frac{1}{2} \ln N \approx \int_1^N \ln x \, dx$$

$$\begin{aligned}
&= [x \ln x - x]_1^N \\
&= N \ln N - N - \ln 1 + 1 \\
&\approx N \ln N - N.
\end{aligned}$$

See appendix A for the integral and appendix B for the trapezium rule. Notice that even for large N $\ln N$ is not that large, for example $\ln 10^{23} = 23 \ln 10 = 52.0 \ll 10^{23}$ so we can't ignore the N term just because the $N \ln N$ term grows slightly faster. Strictly this is an asymptotic approximation meaning that

$$\lim_{N \rightarrow \infty} \frac{N \ln N - N}{N!} = 1.$$

$N!$ and $N \ln N - N$ have been plotted in figure 20.1 for comparison.

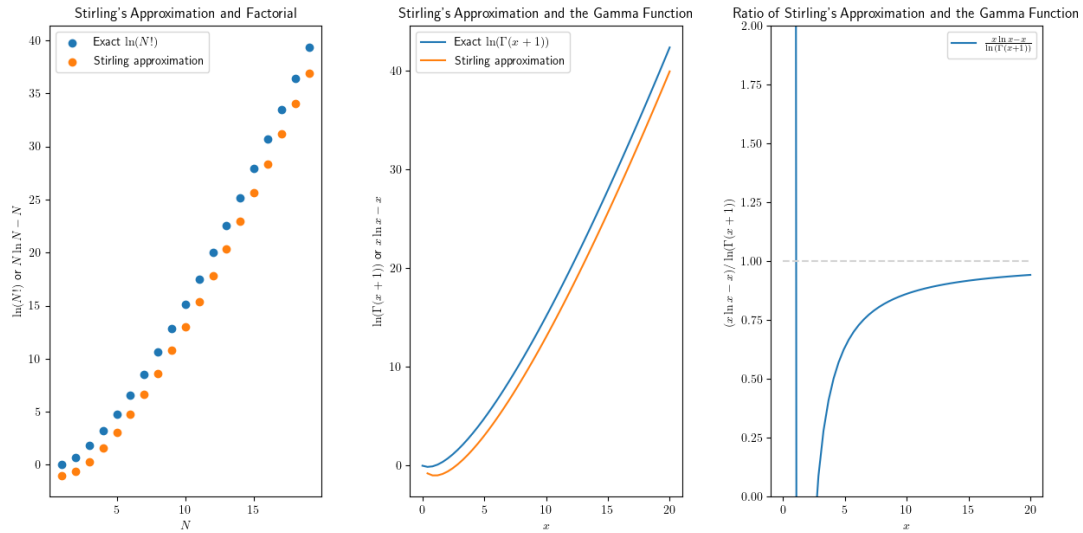


Figure 20.1: Plot of $N!$ and $N \ln N - N$ as well as the continuous extension of the factorial, the Γ function, which is defined such that $\Gamma(N+1) = N!$ for $N \in \mathbb{N}$. Also shown is the ratio $(x \ln x - x) / \Gamma(x+1)$ which tends to 1 as $x \rightarrow \infty$.

N	$\ln(N!)$	$N \ln N - N$	Absolute Error	Percentage Error
2	0.693	-0.614	1.31	189%
3	1.79	0.296	1.50	83.5%
4	3.18	1.55	1.63	51.4%
5	4.79	3.05	1.74	36.4%
6	6.58	4.75	1.83	27.8%
7	8.53	6.62	1.90	22.3%
8	10.6	8.64	1.97	18.6%
9	12.8	10.8	2.03	15.8%
10	15.1	13.0	2.08	13.8%
11	17.5	15.4	2.13	12.1%
12	20.0	17.8	2.17	10.8%
13	22.6	20.3	2.21	9.79%
14	25.2	22.9	2.24	8.91%
15	27.9	25.6	2.28	8.17%
16	30.7	28.4	2.31	7.53%
17	33.5	31.2	2.34	6.99%
18	36.4	34.0	2.37	6.51%
19	39.3	36.9	2.40	6.09%
20	42.3	39.9	2.42	5.72%
50	148.5	145.6	2.88	1.94%
100	364.7	360.5	3.22	0.886%
1000	5912.1	5907.8	4.37	0.0740%

Table 20.1: Some values of $\ln(N!)$ and $N \ln N - N$. The percentage error first falls below 1% at $N = 90$.

21 Probability Part Two

21.1 Poisson Distribution

Using Sterling's approximation we can approximate the binomial coefficient. If $N \gg n$ then

$$\begin{aligned}
 \ln \binom{N}{n} &= \ln \left[\frac{N!}{n!(N-n)!} \right] \\
 &= \ln(N!) - \ln[(N-n)!] - \ln(n!) \\
 &\approx N \ln N - N - (N-n) \ln(N-n) - (N-n) - \ln(n!) \\
 &= N \ln N - (N-n) \ln(N-n) + n - \ln(n!) \\
 &\approx N \ln N - (N-n) \left[\ln N - \frac{n}{N} \right] - \ln(n!) \\
 &= n \ln N + n - \frac{n^2}{N} - \ln(n!) \\
 &\approx n \ln N - \ln(n!)
 \end{aligned}$$

where we have used Stirling's approximation for $\ln(N!)$ and $\ln[(N-n)!]$ and used a Taylor series for $\ln(N-n) \approx \ln N - n/N$. We have also only kept the highest order terms. Thus

$$\binom{N}{n} \approx \exp[n \ln N - \ln(n!)] = \frac{N^n}{n!}.$$

Now consider

$$(1-p)^{N-n} = \exp[(N-n) \ln(1-p)] \approx \exp[-(N-n)p] \approx e^{-Np}.$$

Here we have used $\ln(1-p) \approx -p$ for $p \ll 1$ and $N-n \approx N$. More strictly we require that $N \rightarrow \infty$ and $p \rightarrow 0$ such that $Np = \bar{n}$ is finite¹⁸. Combining these two results we see that

$$P(n) = \binom{N}{n} p^n (1-p)^{N-n} \approx \frac{N^n}{n!} p^n e^{-Np} = (Np)^n \frac{e^{-Np}}{n!} = \bar{n}^n \frac{e^{-\bar{n}}}{n!}.$$

¹⁸For a more rigorous derivation see the statistics part of Fourier analysis and statistics course.

This is the Poisson distribution. It applies when N is large and p is small.

This distribution is already properly normalised:

$$\begin{aligned}\sum_{n=0}^{\infty} P(n) &= \sum_{n=0}^{\infty} \frac{1}{n!} \bar{n}^n e^{-\bar{n}} \\ &= e^{-\bar{n}} \sum_{n=0}^{\infty} \frac{\bar{n}^n}{n!} \\ &= e^{-\bar{n}} e^{\bar{n}} \\ &= 1.\end{aligned}$$

The mean is \bar{n} :

$$\begin{aligned}\sum_{n=0}^{\infty} nP(n) &= \sum_{n=0}^{\infty} n \frac{1}{n!} \bar{n}^n e^{-\bar{n}} \\ &= \sum_{n=1}^{\infty} n \frac{1}{n!} \bar{n}^n e^{-\bar{n}} \\ &= \sum_{n=1}^{\infty} \frac{1}{(n-1)!} \bar{n}^n e^{-\bar{n}} \\ &= \sum_{m=0}^{\infty} \frac{1}{m!} \bar{n}^{m+1} e^{-\bar{n}} \\ &= \bar{n} e^{-\bar{n}} \sum_{m=0}^{\infty} \frac{\bar{n}^m}{m!} \\ &= \bar{n} e^{-\bar{n}} e^{\bar{n}} \\ &= \bar{n}.\end{aligned}$$

The variance is \bar{n} . To show this we use $\overline{\Delta n^2} = \overline{n^2} - \bar{n}^2$. We already know \bar{n} so we just need $\overline{n^2}$. To find this we use the fact that $\overline{n^2} = \overline{n(n-1)} + \bar{n}$. We can find $\overline{n(n-1)}$ as follows:

$$\begin{aligned}\overline{n(n-1)} &= \sum_{n=0}^{\infty} n(n-1)P(n) \\ &= \sum_{n=0}^{\infty} n(n-1) \frac{\bar{n}^n}{n!} e^{-\bar{n}} \\ &= \sum_{n=2}^{\infty} n(n-1) \frac{\bar{n}^n}{n!} e^{-\bar{n}} \\ &= \sum_{n=2}^{\infty} \frac{\bar{n}^n}{(n-2)!} e^{-\bar{n}} \\ &= \sum_{m=0}^{\infty} \frac{\bar{n}^{m+2}}{m!} e^{-\bar{n}} \\ &= \bar{n}^2 e^{-\bar{n}} \sum_{m=0}^{\infty} \frac{\bar{n}^m}{m!} \\ &= \bar{n}^2 e^{-\bar{n}} e^{\bar{n}} \\ &= \bar{n}^2.\end{aligned}$$

Hence

$$\overline{\Delta n^2} = \overline{n^2} - \bar{n}^2 = \overline{n(n-1)} + \bar{n} - \bar{n}^2 = \bar{n}^2 + \bar{n} - \bar{n}^2 = \bar{n}.$$

21.2 Gaussian Distribution

We now consider the case when N is very large and so is Np . For $P(n)$ to not be vanishingly small we need for n to be of the same order as Np . First we define $s(n) = \ln[P(n)]$ and using Stirling's

approximation for all factorials we have

$$\begin{aligned}
 s(n) &= \ln[P(n)] \\
 &= \ln \left[\frac{N!}{n!(N-n)!} p^n (1-p)^{N-n} \right] \\
 &= \ln(N!) - \ln(n!) - \ln[(N-n)!] + n \ln p + (N-n) \ln(1-p) \\
 &\approx N \ln N - N - n \ln n + n - (N-n) \ln(N-n) + N - n + n \ln p + (N-n) \ln(1-p).
 \end{aligned}$$

Computing derivatives for later we have

$$\begin{aligned}
 s'(n) &= -\ln n - 1 + 1 + \frac{N}{N-n} + \ln(N-n) - \underbrace{\frac{n}{N-n} - 1}_{=-N/(N-n)} + \ln(p) - \ln(1-p) \\
 &= \ln p - \ln(1-p) + \ln(N-n) - \ln n \\
 s''(n) &= -\frac{1}{N-n} - \frac{1}{n}.
 \end{aligned}$$

Notice that $s(n)$ is maximised at $n = Np$, i.e. the mean. We now define $x = n - Np$, the deviation from the mean, and expand around this point:

$$s(x) = s(Np) + xs'(Np) + \frac{x^2}{2}s''(Np) + \dots$$

Since s is maximised at $n = Np$ the first derivative will evaluate to zero. Thus

$$s(x) \approx s(Np) - \frac{x^2}{2Np(1-p)}.$$

So

$$P(n) \approx \exp \left[s(Np) - \frac{x^2}{2Np(1-p)} \right] = A \exp \left[-\frac{x^2}{2Np(1-p)} \right]$$

where we absorb the constant $\exp[s(Np)]$ into the normalisation factor, A . Now assuming that this is valid for a continuous variable x we have the PDF

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left[-\frac{(n - \bar{n})^2}{2\sigma^2} \right]$$

where $\sigma^2 = Np(1-p)$. This is the Gaussian distribution. See appendix C for details on the normalisation.

21.3 Large Numbers

In statistical mechanics we often have incredibly large numbers, typically $N \approx 10^{23}$. This is useful for it makes the following approximations *very* accurate.

Let $\{x_i\}$ be N random variables. The **law of large numbers** states that

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N x_i = \bar{x}.$$

Here \bar{x} is the true mean of the distribution that x_i follow. In words this says as sample size increases the sample mean tends towards the population mean. We use this to our advantage as we expect for large N the approximation of the sample mean and population mean being the same will be a very good approximation.

Let $\{x_i\}$ be N random variables drawn from a distribution with mean \bar{x} and variance $\overline{\Delta x^2}$. Then the **central limit theorem** states that the sum

$$S = \sum_{i=1}^N x_i$$

in the limit $N \rightarrow \infty$ will be a random variable drawn from a Gaussian distribution with mean $\bar{S} = N\bar{x}$ and standard deviation $\Delta S^2 = N\Delta x^2$. Notice that this doesn't require individual x_i to follow a Gaussian distribution. Technically not all distributions will tend towards Gaussians but all of the ones we will consider in this course will. One useful consequence of this is that the fractional deviation, σ/μ , always goes as $\sim 1/\sqrt{N}$ so increasing N will have the effect of sharpening the distribution simplifying things further for large N .

21.4 Introductory Statistical Mechanics

21.5 Ensembles

An **ensemble** the system we consider. Typically we distinguish between three different types of ensembles. A **micro-canonical ensemble** is a truly closed system. The number of particles, N , is fixed as is the internal energy, E ¹⁹. The universe is the only true micro-canonical ensemble that exist but many systems can be approximated as micro-canonical ensembles. For example a gas in a box with adiabatic walls is a micro-canonical ensemble however in real life truly adiabatic walls don't exist. A **canonical ensemble** is a system where the number of particles, N , is fixed but the internal energy, E , is not. For example a gas in a box has a fixed number of particles (assuming an air tight box and no quantum tunnelling out of the box) but by colliding with the wall gas molecules can give some of their energy to the box and then to the outside. A **grand-canonical ensemble** has neither n nor E fixed. Essentially these are three different systems with different conservation laws.

Key Point 1

A **microstate** is a complete specification of the state of the system on a microscopic scale.

For example knowing the microstate of a box of gas would involve knowing the position and momentum of each particle which is $6N$ degrees of freedom.

Key Point 2

A **macrostate** is a limited description of the state of the system given by macroscopic (measurable) observables.

For example the macrostate of a box of gas is the pressure, temperature and volume of the gas. Typically each macrostate corresponds to a large number of different microstates which all result in the same macroscopic properties.

We will assume in this course that all systems contain only **weakly interacting** constituents, this is nothing to do with the weak force, it simply means that no energy is stored in internal degrees of freedom, for example a weakly interacting system will have no vibrational energy but will have kinetic energy. Strongly interacting systems, again, nothing to do with the strong force, just the opposite of weakly interacting systems, will be covered in later courses.

22 Entropy

Key Point 3

To any macrostate there corresponds, in general, very many microstates.

The multiplicity, or weight, of a given macrostate is the number of microstates that correspond to that macrostate. We denote the multiplicity of the macrostate with N particles, energy E , and free microscopic parameters, $\{\alpha\}$, by $\Omega(N, E, \{\alpha\})$, or to simplify notation $\Omega(E, \{\alpha\})$ when it is clear that N is constant. The multiplicity of a macrostate can tell us a lot about a system. To see this we will consider an example.

¹⁹In statistical mechanics we use E for internal energy instead of the U used in thermodynamics.

22.1 Model Magnet

We consider a system of independent spins in a uniform magnetic field, \mathbf{H} . The spins can be in one of two states. The ground state, \uparrow , where the spin is aligned with the magnetic field or an excited state, \downarrow , where the spin is anti-aligned with the magnetic field. The corresponding energies are $\varepsilon = -mH$ and $\varepsilon = mH$. We consider the case of N spins with fixed energy E . Let n_1 be the number of spins in the ground state and n_2 be the number of spins in the excited state. Clearly $N = n_1 + n_2$. As well as this the total energy is simply the sum of the energies of each state which is the sum of the energy of the ground and excited states weighted by the number of spins in that state:

$$E = -mHn_1 + mHn_2.$$

We can solve these two equations and find that

$$n_1 = \frac{1}{2} \left(N - \frac{E}{mH} \right), \quad \text{and} \quad n_2 = \frac{1}{2} \left(N + \frac{E}{mH} \right).$$

The exact relationship between n_1 and n_2 and the values N and E isn't important, what is important is that n_1 and n_2 are fixed by fixing N and E . The only thing that can change is which spins are in which state.

The weight of a given macrostate with N particles and energy E is

$$\Omega(N, E) = \binom{N}{n_2} = \frac{N!}{n_1!n_2!}$$

here we have used $N - n_2 = n_1$. To lighten notation we define $n = n_2$ and use $n_1 = N - n$. For an explicit example counting the microstates see tables 22.1 and 22.2. There are a few things to notice

Macrostate	Microstates	Weight
$E = -3mH$	$\uparrow\uparrow\uparrow$	1
$E = -mH$	$\uparrow\uparrow\downarrow$	3
	$\uparrow\downarrow\uparrow$	
	$\downarrow\uparrow\uparrow$	
$E = mH$	$\uparrow\downarrow\downarrow$	3
	$\downarrow\uparrow\downarrow$	
	$\downarrow\downarrow\uparrow$	
$E = 3mH$	$\downarrow\downarrow\downarrow$	1

Table 22.1: The multiplicity of macrostates with $N = 3$ and a given value of E .

Macrostate	Microstates	Weight
$E = -4mH$	$\uparrow\uparrow\uparrow\uparrow$	1
$E = -2mH$	$\uparrow\uparrow\uparrow\downarrow$	4
	$\uparrow\uparrow\downarrow\uparrow$	
$E = 0$	$\uparrow\uparrow\uparrow\downarrow$	6
	$\uparrow\uparrow\downarrow\uparrow$	
	$\uparrow\downarrow\uparrow\uparrow$	
	$\uparrow\downarrow\uparrow\downarrow$	
	$\downarrow\uparrow\uparrow\uparrow$	
	$\downarrow\uparrow\uparrow\downarrow$	
$E = 2mH$	$\downarrow\downarrow\uparrow\uparrow$	4
	$\downarrow\downarrow\uparrow\downarrow$	
$E = 4mH$	$\downarrow\downarrow\downarrow\uparrow$	0
	$\downarrow\downarrow\downarrow\downarrow$	

Table 22.2: The multiplicity of macrostates with $N = 4$ and a given value of E .

here. First the special cases of $n_1 = N$ or $n_2 = N$ always have multiplicity 1 as there is only one way for all spins to be the same. Outside of these cases the numbers increase rapidly. For example for $N = 10$ the multiplicity of the $E = 0$ state, corresponding to $n_1 = n_2 = 5$ is 252 and the multiplicity of the $E = 2mH$ state, corresponding to $n_1 = 4$ and $n_2 = 6$, is 210.

We can approximate the multiplicity for large N using Sterling's approximation assuming that N , n and $N - n$ are large we have

$$\begin{aligned}
 \ln \Omega(N, E) &= \ln \binom{N}{n} \\
 &= \ln \frac{N!}{n!(N-n)!} \\
 &\approx N \ln N - N - n \ln n + n - (N-n) \ln(N-n) + (N-n) \\
 &= N \left[\ln N - \frac{n}{N} \ln n - \left(1 - \frac{n}{N}\right) \ln(N-n) \right] \\
 &= N \left[-\frac{n}{N} \ln \left(\frac{n}{N}\right) - \left(1 - \frac{n}{N}\right) \ln \left(1 - \frac{n}{N}\right) \right].
 \end{aligned}$$

Here we used

$$-\frac{n}{N} \ln \left(\frac{1}{N}\right) - \left(1 - \frac{n}{N}\right) \ln \left(\frac{1}{N}\right) = \frac{n}{N} \ln N + \left(1 - \frac{n}{N}\right) \ln N = \ln N$$

Hence we find that

$$\frac{1}{N} \ln \Omega(N, E) = s\left(\frac{n}{N}\right)$$

where

$$s(x) = -(1-x) \ln(1-x) - x \ln x.$$

This function, s , has several key features:

- It has a maximum at $x = 1/2$
- It is symmetric about $x = 1/2$ since $s(x) = s(1-x)$
- $s(0) = s(1) = 0$, this can be seen by taking limits formally or just noting that as $x \rightarrow 0, 1$ we have a polynomial going to 0 times a log going to $-\infty$. Since polynomials grow faster they will dominate and we will have $s(x) = 0$.
- Since $\Omega = e^{Ns(n/N)}$ the weight function is exponential in N but $\ln \Omega$ is proportional to N .

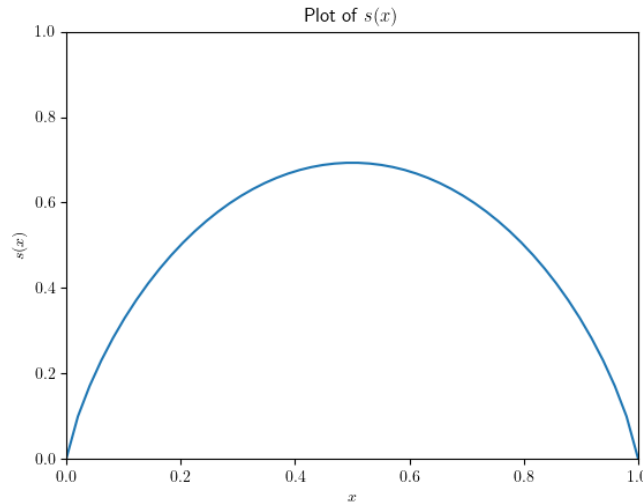


Figure 22.1: A plot of $s(x) = -(1-x) \ln(1-x) - x \ln x$.

At the start of this system we mentioned a free microscopic variable α . This is a microscopic property that is not fixed by choosing a particular macroscopic state. For example if we line up the spins in our system then we could define the free microscopic variable n_L being the number of excited dipoles on the left hand side and n_R being the number of excited dipoles on the right hand side. These values are constrained by $n_L + n_R = n$ but we still have one degree of freedom left so we are free to pick n_L to be any integer from zero to $N/2$.

To calculate the multiplicity of a given macrostate with some value of n_L we simply consider two separate subsystems made of the left and right halves and count the number of ways we can have n_L excited states in the left hand side and $n_R = n - n_L$ excited states in the right hand side. Since the two halves are independent the total number of ways we can have n_L excited states in the left hand side is

$$\Omega(N, E, n_L) = \binom{N/2}{n_L} \binom{N/2}{n - n_L}.$$

In the case that $E = 0$ and so $n = N/2$ and $n_L = N/2 - n_R$ it can be shown that

$$\frac{1}{N} \ln \Omega(N, 0, n_L) \approx s \left(\frac{n_L}{N/2} \right).$$

Key Point 4

We define the entropy of a system as

$$S(N, E, \{\alpha\}) = k_B \ln \Omega(N, E, \{\alpha\}).$$

Here $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$ is Boltzmann's constant.

The entropy of a macrostate of our model magnet is then $k_B N s(n/N)$.

We now know a lot about the weight function so why is it important? The reason lies in the following assumption:

Key Point 5

An isolated system is equally likely to be found in any of its allowed microstates.

This is a reasonable assumption and is almost always at least a good approximation. This is referred to as the principle of equal a priori probabilities. This assumption is essentially due to assuming equal probabilities before a Bayesian calculation of the most likely state. Having no further information this really is the best guess.

Key Point 6

Assuming all microstates are equally likely the probability that an isolated system will be found in the macrostate $N, E, \{\alpha\}$ is proportional to $\Omega(N, E, \{\alpha\})$.

This is simply due to all microstates being equally likely so the only thing biasing a system towards a particular macrostate is what proportion of all microstates correspond to that macrostate.

The weight function for the model magnet very quickly becomes a sharp spike at $n = N/2$. This means that the most likely state for the model magnet is half of the spins excited and half in the ground state. This assumes that all microstates are allowed which is the case as long as there is at least NmH energy available to the system. Free macroscopic variables settle into an equilibrium value that maximises Ω simply through the sheer overwhelming probability of the microstates with these values.

This is a pretty amazing result. The system of spins is completely isolated and each spin is independent of all other spins yet for sufficiently large N we can say that approximately $N/2$ spins will be in each state.

One way to view a system is as randomly walking through parameter space moving from microstate to microstate. On average each move it makes will take it to a more likely macrostate until eventually it is in the most likely macrostate. It is then unlikely to change much, it is in equilibrium. While the system moves between microstates with each macrostate becoming more likely it must also be moving from lower multiplicity states to higher multiplicity states. Thus the entropy is increasing. We see that this definition of entropy satisfies the second law of thermodynamics in that it increases with every process. The fact that this is a law comes down to the huge size of N most of the time which means that moving to a less likely macrostate (and hence decreasing entropy) is so unlikely it simply doesn't happen. Recall that deviations from the mean are of the order $N^{-1/2}$ and therefore miniscule.

23 The Boltzmann Distribution

23.1 Addition of Entropy

Consider a system split into two subsystems, 1 and 2. If each subsystem has N_i particles and energy E_i then the total number of microstates with $N = N_1 + N_2$ for some specific N_i and energy $E = E_1 + E_2$ for some specific E_i and some other parameters, $\{\alpha\}$, is

$$\Omega(N, E, \{\alpha\}) = \Omega_1(N_1, E_1, \{\alpha\})\Omega_2(N_2, E_2, \{\alpha\}).$$

Here Ω_i is the weight function for each subsystem. The entropy of the whole system is then

$$\begin{aligned} S(N, E, \{\alpha\}) &= k_B \ln \Omega(N, E, \{\alpha\}) \\ &= k_B \ln [\Omega_1(N_1, E_1, \{\alpha\})\Omega_2(N_2, E_2, \{\alpha\})] \\ &= k_B \ln \Omega_1(N_1, E_1, \{\alpha\}) + k_B \ln \Omega_2(N_2, E_2, \{\alpha\}) \\ &= S_1(N_1, E_1, \{\alpha\}) + S_2(N_2, E_2, \{\alpha\}) \end{aligned}$$

where S_i are the entropies of the individual subsystems.

23.2 Entropy and Temperature

Consider a system with fixed N split into two subsystems. If the energy of these subsystems is E_i and the energy of the whole system is $E = E_1 + E_2$ then the total entropy is

$$S(E) = S_1(E_1) + S_2(E_2)$$

where we drop N from the notation as it is constant. Suppose we want to now what the effect of changing E_1 to $E_1 + dE_1$. Since E is fixed this change necessitates changing E_2 to $E_2 - dE_1$. The change in entropy is then

$$\begin{aligned} dS &= dS_1 + dS_2 \\ &= \frac{\partial S_1}{\partial E_1} dE_1 + \frac{\partial S_2}{\partial E_2} dE_2 \\ &= \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) dE_1. \end{aligned}$$

Since entropy is maximised at equilibrium we must have $dS = 0$ and therefore

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}.$$

Recall from the zeroth law of thermodynamics we know that two systems in thermal equilibrium have the same temperature. Therefore it is reasonable to conclude that $\partial S/\partial E$ is some function of T . In fact the correct function is

Key Point 7

$$\frac{\partial S}{\partial E} = \frac{1}{T}.$$

We will justify this later.

Now consider what happens if we change the temperatures of the two systems and then put them in thermal contact. We know from the second law that we must have $dS > 0$ so

$$dS = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) dE_1 = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 > 0.$$

If $T_1 > T_2$ then this will be true only if dE_1 is negative and therefore energy flows from the hotter system to the cooler system. If $T_1 < T_2$ then dE_1 is positive and therefore energy still flows from hot to cold.

23.3 The Boltzmann Distribution

The setup that we consider is a heat bath at temperature T_b and a system in the heat bath. The system we consider has N_s particles which is fixed. Its energy is not fixed. The composite system (system and heat bath), or the universe, has both N and E_{tot} fixed. The composite is thus isolated and has fixed total energy so all microstates are equally likely. However we are interested in the microstates of the system which we will see are not all equally likely.

Suppose the system is in a microstate with energy E_i . We want to know the probability, $P(E_i)$, of the system being in this microstate. Notice that if the system has energy E_i then the bath must have energy $E_b = E_{\text{tot}} - E_i$. Thus

$$P(E_i) = \frac{\Omega(E_i)\Omega_b(E_{\text{tot}} - E_i)}{\Omega_{\text{universe}}(E_{\text{tot}})}.$$

Here $\Omega(E_i)$ gives the number of ways to get the *microstate* with E_i . Therefore $\Omega(E_i) = 1$. Also Ω_b is the weight system for the bath and Ω_{universe} is the weight function for the composite. The important part of this equation is $\Omega_b(E_{\text{tot}} - E_i)$ since Ω_{universe} is a constant and we can therefore discard it and recover the information by requiring P be normalised. Thus

$$P(E_i) \propto \Omega_b(E_{\text{tot}} - E_i).$$

We can express Ω_b in terms of the entropy, S_b , of the bath:

$$\Omega_b(E_{\text{tot}} - E_i) = \exp \left[\frac{S_b(E_{\text{tot}} - E_i)}{k_B} \right].$$

We assume that $E_i \ll E_{\text{tot}}$ and therefore we can Taylor expand the entropy as

$$S_b(E_{\text{tot}} - E_i) = S_b(E_{\text{tot}}) - E_i \left. \frac{\partial S_b}{\partial E_b} \right|_{E_{\text{tot}}} + \frac{E_i^2}{2} \left. \frac{\partial^2 S_b}{\partial E_b^2} \right|_{E_{\text{tot}}} + \dots.$$

As usual we only keep the first two terms, we will show later that the second term is small. Thus

$$\begin{aligned} P(E_i) &\propto \exp \left[\frac{S_b}{k_B} - \left. \frac{\partial S_b}{\partial E_b} \right|_{E_{\text{tot}}} \frac{E_i}{k_B} \right] \\ &= \exp \left[\frac{S_b}{k_B} \right] \exp \left[- \left. \frac{\partial S_b}{\partial E_b} \right|_{E_{\text{tot}}} \frac{E_i}{k_B} \right] \\ &\propto \exp \left[- \left. \frac{\partial S_b}{\partial E_b} \right|_{E_{\text{tot}}} \frac{E_i}{k_B} \right] \\ &= \exp \left[- \frac{E_i}{k_B T} \right] \end{aligned}$$

This is the Boltzmann factor. We now require P to be normalised so

$$\sum_{\text{all microstates}} P(E_i) = \sum_{\text{all microstates}} \text{const.} e^{-E_i/k_B T} = 1.$$

Key Point 8

The probability that a system is in a microstate with energy E_i is

$$P(E_i) = \frac{e^{-E_i/k_B T}}{Z}$$

where

$$Z = \sum_{\text{all microstates}} e^{-E_j/k_B T}.$$

Z is known as the statistical sum or partition function.

This is quite a remarkable result. The only information about a microstate that we need is the energy and the temperature. For example if we consider particles in an isothermal atmosphere with mass m then the height is distributed as

$$P(h) = \frac{1}{Z} \exp \left[-\frac{mgh}{k_B T} \right].$$

If instead we are considering particles in a gas then the velocity in the x direction is distributed as

$$P(v_x) = \frac{1}{Z} \exp \left[-\frac{mv_x^2}{2k_B T} \right].$$

Example 23.1. Consider a single particle with magnetic moment m in a magnetic field, H , Suppose the particle can be either spin up, with energy $E_{\uparrow} = -mH$, or spin down, with energy $E_{\downarrow} = mH$. Then

$$\begin{aligned} Z &= \exp \left[-\frac{E_{\uparrow}}{k_B T} \right] + \exp \left[-\frac{E_{\downarrow}}{k_B T} \right] \\ &= \exp \left[\frac{mH}{k_B T} \right] + \exp \left[-\frac{mH}{k_B T} \right] \\ &= 2 \cosh \left(\frac{mH}{k_B T} \right). \end{aligned}$$

So the probability of being in the spin up state is

$$\begin{aligned} P(\uparrow) &= \frac{\exp \left[\frac{mH}{k_B T} \right]}{2 \cosh \left(\frac{mH}{k_B T} \right)} \\ &= \frac{1}{1 + \exp \left[-\frac{2mH}{k_B T} \right]}. \end{aligned}$$

Now consider what happens at $T = 0$. We see that $P(\uparrow) = 1$. This is because if there is no thermal energy then we expect to find the system in the ground state. Then as $T \rightarrow \infty$ we find that $P(\uparrow) \rightarrow 1/2$. This is because as the total energy available increases the small energy difference between the two states becomes negligible and both states become equally likely.

We can also calculate the average energy:

$$\begin{aligned} \bar{E} &= E_{\uparrow} P(\uparrow) + E_{\downarrow} P(\downarrow) \\ &= \frac{1}{Z} \left(-mH \exp \left[\frac{mH}{k_B T} \right] + mH \exp \left[-\frac{mH}{k_B T} \right] \right) \\ &= -mH \frac{\sinh \left(\frac{mH}{k_B T} \right)}{2 \cosh \left(\frac{mH}{k_B T} \right)} \\ &= -mH \tanh \left(\frac{mH}{k_B T} \right). \end{aligned}$$

Recall that for small x we have $\tanh x \approx x$ and for large x $\tanh x \approx 1$. Therefore we expect \bar{E} to increase exponentially from $-mH$ with T for low temperatures before tapering off at 0 for high temperatures.

Now consider the entropy of the model magnet:

$$S(E) = -Nk_B [x \ln x + (1-x) \ln(1-x)]$$

where

$$x = \frac{n}{N} = \frac{1}{2} \left(1 + \frac{E}{NmH} \right).$$

Where N is the total number of dipoles and n is the number of excited dipoles. We find that

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$

$$\begin{aligned}
&= \frac{\partial x}{\partial E} \frac{\partial S}{\partial x} \\
&= -\frac{Nk}{2NmH} [\ln x + 1 - \ln(1-x) - 1] \\
&= -\frac{k_B}{2mH} \ln \left(\frac{x}{1-x} \right).
\end{aligned}$$

So we find that

$$\exp \left(-\frac{2mH}{k_B T} \right) = \frac{x}{1-x}$$

which means

$$x = \frac{n}{N} = \frac{\exp \left(-\frac{2mH}{k_B T} \right)}{1 + \exp \left(-\frac{2mH}{k_B T} \right)} = \frac{\exp(-\beta mH)}{\exp(\beta mH) + \exp(-\beta mH)}$$

where $\beta = 1/k_B T$. Taking a frequentist view n/N is the probability that a single dipole is in an excited state so we see that we recover the Boltzmann distribution for a single dipole. This initially seems wrong as we would expect an isolated system to have all microstates be equally likely. However this isn't an isolated system. The single dipole in the model magnet can exchange energy with the other $N-1$ dipoles so we can treat a single dipole as a canonical system in a heat bath made of the other $N-1$ dipoles.

During this derivation we neglected the second order term. We will now see that this is an extremely valid thing to do:

$$\begin{aligned}
\frac{E_i^2}{2} \frac{\partial^2 S_b}{\partial E_b^2} &= \frac{E_i^2}{2} \frac{\partial}{\partial E_b} \frac{1}{T_b} \\
&= -\frac{E_i^2}{2T_b} \frac{\partial T_b}{\partial E_b} \\
&\propto \frac{1}{C_b}
\end{aligned}$$

where $C_b = \partial E_b / \partial T_b$ is the heat capacity of the bath. By definition the heat capacity of a heat bath is very large as the temperature must remain constant. Ideally it is infinite. This means that the second order term is, even in the real world, very small and can safely be neglected.

24 Free Energy Minimisation

24.1 Energy Fluctuations

The mean energy of a canonical system is

$$\bar{E} = \sum_i E_i P(E_i)$$

where the sum is over all microstates

$$= \frac{1}{Z} \sum_i E_i \exp \left(-\frac{E_i}{k_B T} \right)$$

introducing $\beta = 1/k_B T$ this becomes

$$\begin{aligned}
&= \frac{1}{Z} \sum_i E_i e^{-\beta E_i} \\
&= \frac{1}{Z} \sum_i \frac{\partial}{\partial \beta} e^{-\beta E_i} \\
&= -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i} \\
&= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\
&= -\frac{\partial}{\partial \beta} \ln Z.
\end{aligned}$$

So

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial T}{\partial \beta} \frac{\partial \ln Z}{\partial T} = k_B T^2 \frac{\partial \ln Z}{\partial T} \quad (24.1)$$

Considering now the heat capacity, C , we have

$$C = \frac{\partial \bar{E}}{\partial T}.$$

To calculate this we use

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} = \left(\frac{\partial}{\partial T} \frac{1}{k_B T} \right) \frac{\partial}{\partial \beta} = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta}$$

so

$$C = -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \frac{\sum_i E_i e^{-\beta E_i}}{Z}$$

taking care as Z has β dependence and applying the product rule this gives

$$\begin{aligned} &= -\frac{1}{k_B T^2} \left[-\frac{\sum_i E_i^2 e^{-\beta E_i}}{Z} - \frac{\sum_i E_i e^{-\beta E_i}}{Z^2} \frac{\partial Z}{\partial \beta} \right] \\ &= -\frac{1}{k_B T^2} \left[-\sum E_i^2 P(E_i) - \sum_i E_i P(E_i) \frac{\partial Z}{\partial \beta} \frac{1}{Z} \right] \\ &= \frac{1}{k_B T^2} (\overline{E^2} - \bar{E}^2) \\ &= \frac{\Delta E^2}{k_B T^2}. \end{aligned}$$

Here we have used

$$\sum_i E_i P(E_i) = \bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}, \quad \text{and} \quad \sum_i E_i^2 P(E_i) = \overline{E^2}.$$

The heat capacity characterises the response of the system to a change of temperature. We see here that this responds is proportional to the size of energy fluctuations that the system can undergo. Notice that $\bar{E} \propto N$ and therefore $C \propto N$ which means that $\Delta E^2 \propto N$. Thus the size of fluctuations on the scale of the mean energy is

$$\frac{\sqrt{\Delta E^2}}{\bar{E}} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}.$$

This is exactly what we would expect. We see that even though E is free to change in a canonical system for large N the energy distribution is still sharply peaked at \bar{E} .

24.2 Free Energy

Previously we have considered $P(E_i)$, the probability that the system is in a *microstate* with energy E_i . Now we will consider $P(E)$, the probability that the system is in a *macrostate* with energy E . Before our partition function was

$$Z = \sum_{\text{all microstates}} e^{-E_i/k_B T}.$$

Now this doesn't change but we instead can express it as

$$Z = \sum_{\text{all macrostates}} \Omega(E) e^{-E/k_B T}.$$

These are essentially equivalent but we collapse all microstates with the same energy into one term and weight it with $\Omega(E)$. Thus

$$P(E) = \frac{1}{Z} \Omega(E) e^{-E/k_B T}$$

which again follows from considering each possible microstate with energy $E_i = E$ and combining them into one by weighting the term by $\Omega(E)$.

Inverting the definition of entropy we know that

$$\Omega(E) = e^{S(E)/k_B}.$$

Hence

$$\begin{aligned} P(E) &= \frac{1}{Z} \Omega(E) \exp \left[-\frac{E}{k_B T} \right] \\ &= \frac{1}{Z} \exp \left[\frac{S(E)}{k_B} \right] \exp \left[-\frac{E}{k_B T} \right] \\ &= \frac{1}{Z} \exp \left[\frac{S(E)}{k_B} - \frac{E}{k_B T} \right] \\ &= \frac{1}{Z} \exp \left[-\frac{E - TS(E)}{k_B T} \right] \\ &= \frac{1}{Z} \exp \left[-\frac{F(E)}{k_B T} \right]. \end{aligned}$$

So we see that the probability of finding the system in a macrostate with energy E is directly linked to the Helmholtz free energy, $F(E) = E - TS(E)$. More than this we see that $P(E)$ peaks when the argument of the exponent is maximised meaning that $F(E)$ is minimised.

This gives us a strong general concept:

Key Point 9

The equilibrium values of the macroscopic properties, E and $\{\alpha\}$ of a system in equilibrium are such as to minimise the free energy, $F(E, \{\alpha\}) = E - TS(E, \{\alpha\})$.

This allows us to view the process of coming to equilibrium as a fight between minimising E and maximising S . For example at low temperatures ice forms because the energetically favourable crystal structure outweighs the decrease in entropy (of the system, total entropy still increases). At higher temperatures entropy considerations win out and the less organised water phase dominates.

25 The Partition Function

25.1 Energy, Free Energy, and Entropy from the Partition Function

Recall that we can write

$$Z = \sum_E \Omega(E) e^{-E\beta}$$

where the sum is over the energies of macrostates. The majority of energies fall into a range $\Delta E = \sqrt{\Delta E^2}$ either side of \bar{E} . Since \bar{E} is $\mathcal{O}(N)$ and ΔE is $\mathcal{O}(\sqrt{N})$ this means that the partition function becomes sharply peaked at \bar{E} for large N . This allows us to write

$$\begin{aligned} Z &\approx \Omega(\bar{E}) e^{-\bar{E}\beta} \mathcal{O}(\sqrt{N}) \\ &= e^{-F(T)\beta} \mathcal{O}(\sqrt{N}). \end{aligned}$$

We can treat the free energy, $F = E - TS$, as purely a function of temperature since it depends on T , E , and S , but \bar{E} and S depends only on T at equilibrium. Taking logs we have

$$\ln Z = -\beta F(T) + \mathcal{O}(\sqrt{N}).$$

Neglecting the last term as it is relatively small for large N we have

$$F(T) = \bar{E} - TS(T) = -k_B T \ln Z.$$

This is a very useful formula for calculating the free energy. We can rewrite it in terms of the entropy to get

$$S(T) = k_B \ln Z + \frac{\bar{E}}{T}.$$

Combining this with equation 24.1,

$$E(T) = k_B T^2 \frac{\partial \ln Z}{\partial T},$$

we see that the partition function and temperature alone give us probably the three most important quantities in statistical mechanics.

Key Point 10

$$\begin{aligned} F(T) &= -k_B T \ln Z, \\ E(T) &= k_B T^2 \frac{\partial}{\partial T} \ln Z, \\ S(T) &= k_B \ln Z + \frac{E(T)}{T}. \end{aligned}$$

25.2 Factorisation of the Partition Function

Consider a weakly interacting system. That is a system of particles where the energy of a particle depends only on its position and momentum, there is no energy stored in internal degrees of freedom. Suppose there are N particles with energies ε_i . Then for a we can write the energy of a given microstate as

$$E_r = \varepsilon_{i_1} + \varepsilon_{i_2} + \cdots + \varepsilon_{i_N}.$$

The partition function is then

$$\begin{aligned} Z &= \sum_r e^{-\beta E_r} \\ &= \sum_{i_1, i_2, \dots, i_N} \exp[-\beta(\varepsilon_{i_1} + \varepsilon_{i_2} + \cdots + \varepsilon_{i_N})] \\ &= \left[\sum_{i_1} e^{-\beta \varepsilon_{i_1}} \right] \left[\sum_{i_2} e^{-\beta \varepsilon_{i_2}} \right] \cdots \left[\sum_{i_N} e^{-\beta \varepsilon_{i_N}} \right] \\ &= [Z(1)]^N \end{aligned}$$

where $Z(1)$ is the partition function for a single particle. Using this we have

$$\ln Z = N \ln[Z(1)]$$

which allows us to easily compute F , E , and S . For example

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = -N \frac{\partial}{\partial \beta} \ln[Z(1)] = N \bar{\varepsilon}.$$

Another useful thing that we get from this factorisation is that if we are only interested in particle one then we can sum out all the other states:

$$\begin{aligned} P_{i_1} &= Z^{-1} \sum_{i_2, \dots, i_N} \exp(-\beta[\varepsilon_{i_1} + \varepsilon_{i_2} + \cdots + \varepsilon_{i_N}]) \\ &= \frac{\exp(-\beta \varepsilon_{i_1}) [Z(1)]^{N-1}}{[Z(1)]^N} \\ &= \frac{\exp(-\beta \varepsilon_{i_1})}{Z(1)}. \end{aligned}$$

Key Point 11

For a system of N weakly interacting, distinguishable particles the partition function is

$$Z = [Z(1)]^N$$

and the probability a given particle is in a state with energy ε_i is

$$P(\varepsilon_i) = \frac{\exp(-\beta\varepsilon_i)}{Z(1)}.$$

25.3 The Model Magnet

Earlier we calculated the partition function for a single dipole. It was

$$Z(1) = 2 \cosh x, \quad \text{where} \quad x = \frac{mH}{k_B T}.$$

Using the results we have found in this section we have

$$\begin{aligned} \bar{E} &= N\bar{\varepsilon} \\ &= -N \frac{\partial}{\partial \beta} \ln Z(1) \\ &= -NmH \frac{\partial}{\partial x} \ln Z(1) \\ &= -NmH \tanh x, \\ S(T) &= k_B \ln Z + \frac{\bar{E}}{T} \\ &= Nk_B \ln Z(1) + \frac{N\bar{\varepsilon}}{T} \\ &= Nk_B [\ln(e^x + e^{-x}) - x \tanh x]. \end{aligned}$$

It can be shown that the mean magnetisation is

$$\bar{M} = Nm \tanh x.$$

Considering the function \tanh at extremes as $x \rightarrow 0$ we have

$$\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} \approx \frac{(1+x) - (1-x)}{(1+x) + (1-x)} = x.$$

As $x \rightarrow \infty$ instead we have

$$\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} \approx \frac{e^x}{e^x} = 1.$$

Hence or low fields, i.e. $mH \ll k_B T$ and $x \ll 1$, we have

$$\bar{M} \approx \frac{Nm^2 H}{k_B T}.$$

Or for high fields, i.e. $mH \gg k_B T$ and $x \gg 1$, we have

$$\bar{M} \approx Nm.$$

The susceptibility is defined as

$$\chi_M = \frac{\partial \bar{M}}{\partial H}.$$

Suppose we are interested in the zero-field susceptibility so

$$\chi_M = \left. \frac{\partial \bar{M}}{\partial H} \right|_{H=0} = \frac{Nm^2}{k_B T}.$$

The $1/T$ dependence of χ_M is called the Curie law. Consider the heat capacity with a constant field:

$$\begin{aligned} C_H &= \left(\frac{\partial \bar{E}}{\partial T} \right)_H \\ &= \left(\frac{\partial x}{\partial T} \right)_H \left(\frac{\partial \bar{E}}{\partial x} \right)_H \\ &= N k_B x^2 \operatorname{sech}^2 x. \end{aligned}$$

The behaviour of this at low temperatures, i.e. large x , is

$$\operatorname{sech} x = \frac{2}{e^x + e^{-x}} \approx \frac{2}{e^x} = 2e^{-x}.$$

So we see that at low temperatures the heat capacity will vanish. This is actually a feature of all heat capacities. At $T = 0$ all particles will be in the ground state and they can't leave until $k_B T$ is comparable with the energy of the lowest energy excited state. This means that the temperature can increase up to this point without the energy changing.

26 Strongly Interacting Systems

This section is non-examinable.

Previously we saw that a system which moves to equilibrium minimises the free energy, $F = E - TS$, in the process. This leads to two different behaviours depending on temperature:

- At high temperatures $F \approx -TS$ and minimising F is equivalent to maximising S . This favours high disorder states such as gases.
- At low temperatures $F \approx E$ and minimising F is equivalent to minimising E . This favours low disorder states such as crystals.

At some point we must therefore have a phase transition between the two points. Figure 26.1 shows an

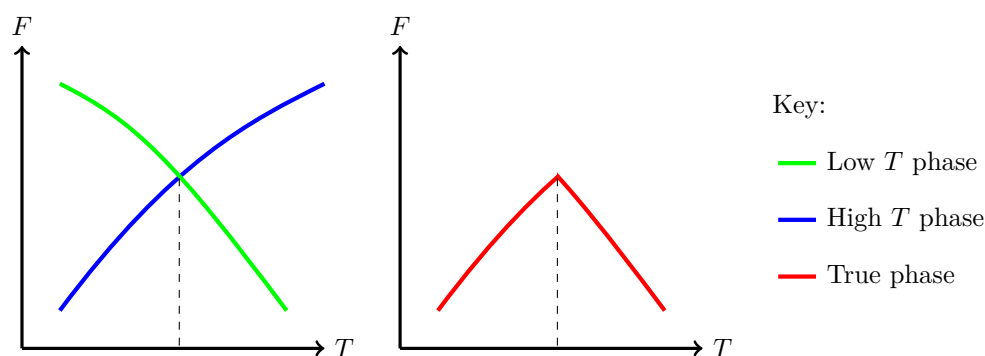


Figure 26.1: The free energy of a low temperature phase and high temperature phase and the free energy of the stable phase.

example of the free energy of two phases preferred at different temperatures and the free energy of the actual phase at any particular temperature. The problem that we see at the transition temperature the free energy is not differentiable. However we previously showed that the free energy is given by

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

so for a non-differentiable point in F we must have something non-analytic in Z . But

$$Z = \sum_i e^{-E_i/k_B T}$$

is surely analytic. This caused a problem for a long time in statistical mechanics until a model was found that could reproduce the expected non-analyticity.

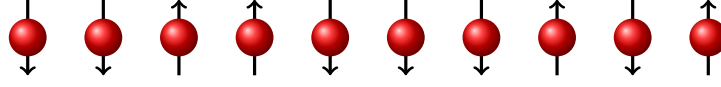


Figure 26.2: The Ising model in one dimension.

26.1 The Ising Model

The Ising model is similar to the model magnet that we have been using. The difference is the Ising model is strongly interacting. In the Ising model we imagine a lattice of spins which can be either up, $+1$, or down, -1 . The spins are not in an external field so for a single particle both spin up and spin down have the same energy. The new feature here is we allow the spins to interact. This lowers the energy if spins align and decreases the energy if they are anti-aligned. Since spin is quantum mechanical it is reasonable to assume that its effects are short ranged and we only consider the direct neighbours of a particle when considering its energy.

26.2 One-Dimensional Ising Model

The simplest case of the Ising model is in one dimension. In this case we have a line of particles with spin up or down and we assume that only the particle on the left and right of a particle effect its energy. Let the spin of the i th particle be S_i . Then a particle with spin J has energy

$$\mathcal{H} = -J \sum_{i,j} S_i S_j$$

where the sum is over the nearest neighbours. The partition function can then be written as

$$\begin{aligned} Z &= \sum_{\text{all microstates}} e^{-E_i/k_B T} \\ &= \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \cdots \sum_{S_N=\pm 1} \exp \left[-\frac{J}{k_B T} (S_1 S_2 + S_2 S_3 + \cdots + S_{N-1} S_N) \right] \\ &= \sum_{S_i, S_j=\pm 1} \exp \left[-\frac{J}{k_B T} (S_1 S_2 + S_2 S_3 + \cdots + S_{N-1} S_N) \right]. \end{aligned}$$

Now define $\sigma_i = S_{i-1} S_i$. The possible values of σ_i , using \pm to denote spin up/down, are

S_{i-1}	S_i	σ_i
+	+	+
+	-	-
-	+	-
-	-	+

Using this we can rewrite the sum that appears in the exponent of the partition function:

$$S_1 S_2 + S_2 S_3 + S_3 S_4 + \cdots + S_{N-1} S_N = \sigma_2 + \sigma_3 + \sigma_4 + \cdots + \sigma_N.$$

Notice that there are $N - 1$ terms in this sum. This is the number of degrees of freedom of the system. The partition function can then be written as

$$Z = \sum_{\sigma_i=\pm 1} \exp \left[-\frac{J}{k_B T} (\sigma_2 + \sigma_3 + \cdots) \right].$$

We can write the partition function for a single particle as

$$Z(1) = \sum_{\sigma} \exp \left[-\frac{J}{k_B T} \sigma \right]$$

and so the partition function for all particles is this to the power of the number of degrees of freedom:

$$Z = [Z(1)]^{N-1}$$

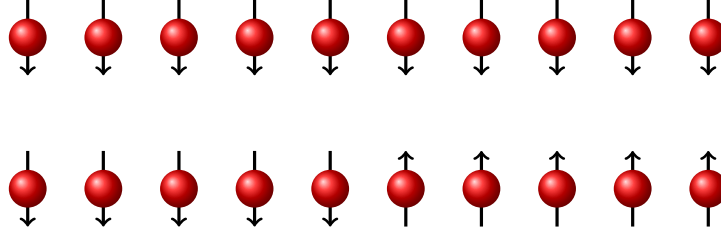


Figure 26.3: The Ising model in one dimension. A completely ordered state (above) and a state with a single defect (below).

$$\begin{aligned}
 &= \left[\sum_{\sigma} \exp \left(-\frac{J}{k_B T} \sigma \right) \right]^{N-1} \\
 &= \left[2 \exp \left(\frac{J}{k_B T} \right) + 2 \exp \left(-\frac{J}{k_B T} \right) \right]^{N-1} \\
 &= 4^{N-1} \left[\cosh \left(\frac{J}{k_B T} \right) \right]^{N-1}
 \end{aligned}$$

where we expand the sum over σ to account for all four possible cases of values of σ , two of which are $+$ and two of which are $-$.

This partition function is analytic. It does not permit phase transitions. This means that the one-dimensional Ising model doesn't have phase transitions. The reason for this comes from considering what possible phases could be. The most obvious is a total ordered state where all spins are up or all spins are down. See figure 26.3. In this case the energy is minimal as all spins are aligned but the entropy is also very low. We introduce a single defect by choosing a particle and flipping the spins of all particles to the right of it. There is only one point where nearest neighbours are unaligned and so the energy is still low. However there are N different particles we could choose to be the first to flip (strictly we are picking a gap between particles and there are $N - 1$ of these but $N - 1 \approx N$ for sufficiently large N). The entropy change then is proportional to N and so the change in free energy is

$$\Delta F = 2J - k_B T N.$$

The second term dominates and this is a large decrease in free energy. The same logic applied again and again can convince us that the state that minimises the free energy is the most disordered state where all spins are aligned randomly. The fact that the most disordered state is also the most favourable means that there are no phase transitions as any single change simply results in a different but still highly disordered state.

26.3 Two-Dimensional Ising Model

The Ising model in two dimensions is mathematically harder to deal with and therefore we will just discuss important results. If there are N total particles and N_{\uparrow} are in the spin up state then there must be $N - N_{\uparrow} = N_{\downarrow}$ particles in the spin down state. Further the net magnetisation of the system is $m = N_{\uparrow} - N_{\downarrow}$. Since the entropy depends only on how many different ways we can split the system into N_{\uparrow} spin up particles and N_{\downarrow} spin down particles we can use the same entropy function as we did with the model magnet. That is

$$S = k_B \ln \binom{N}{N_{\uparrow}} = -k_B N \ln \left[\frac{m+1}{2} \ln \frac{m+1}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \right].$$

This is written here in terms of $m = N_{\uparrow} - N_{\downarrow}$.

Again the energy of a particle depends only on its nearest neighbours but this now includes the particles directly above and below. The energy of a given particle is

$$\mathcal{H} = -J \sum_{i,j} S_i S_j$$

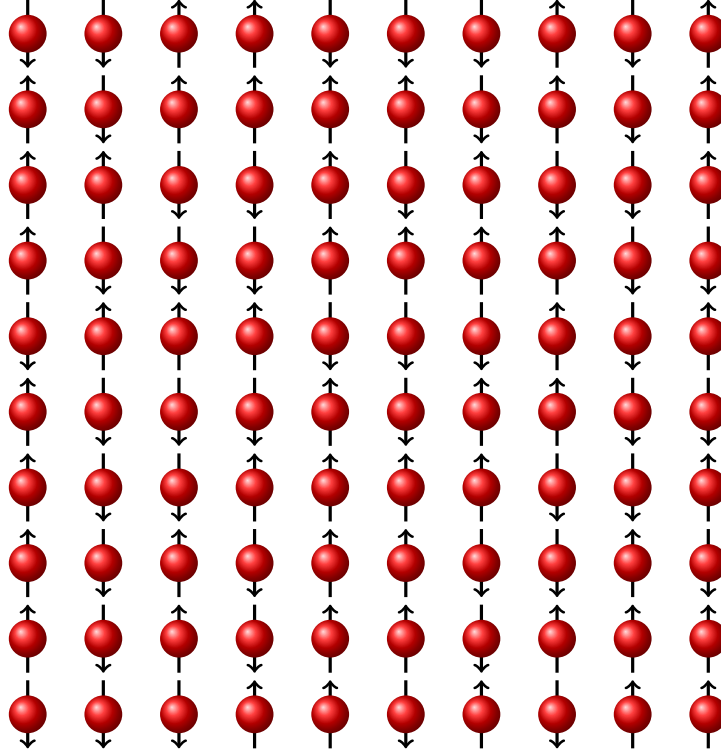


Figure 26.4: The Ising model in two dimensions.

where all symbols have the same meaning as in the one dimensional case and the sum is over the nearest neighbours.

We now apply a mean field theory. This is a fancy way of saying we assume that all of the particles, apart from the particle we are focused on, have the mean value of any property. This means that the energy of a given particle is simply

$$\mathcal{H} = -4Jm^2.$$

The total energy of the system is then the sum of the energy of each particle but we have to introduce a factor of $1/2$ as we are double the contribution of a pair of particles to the energy. Thus

$$E = -2NJm^2$$

The free energy is then

$$F = -2NJm^2 + k_B T N \ln \left[\frac{m+1}{2} \ln \frac{m+1}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \right].$$

It can be shown that the free energy is minimised if

$$m = \tanh \frac{4Jm}{k_B T}.$$

Notice that m appears on the left hand side and also in the argument of \tanh . This introduces non-analyticity which allows for phase transitions in the two dimensional Ising model. The two phases can be shown to be a low temperature phase which favours spins aligned and the plane separates into regions of mostly spin up or mostly spin down, and a high temperature phase which favours disorder and the spin of any one particle is uncorrelated with the spin of its neighbours.

27 Einstein Model of a Crystal

27.1 Classical Model of a Crystal

Crystals are often modelled as a lattice of atoms connected by springs, as shown in figure 27.1. The

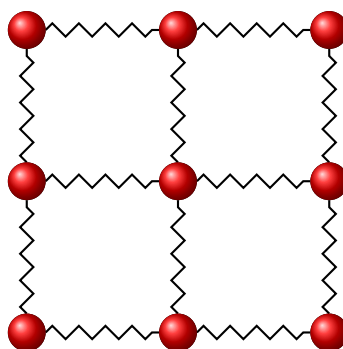


Figure 27.1: A crystal modelled as a lattice of atoms connected by springs.

problem with this model is that it is strongly interacting. What we can do is consider the potential that every particle is in due to its interactions with its neighbours and then model a crystal as a lattice of particles in potentials with no interactions between particles. This removes the strongly interacting component of the model while keeping much of the same physics. Each atom can be approximated as a harmonic oscillator such as in figure 27.2. To start with we will consider this system classically. The

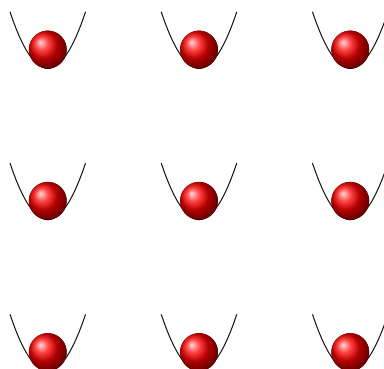


Figure 27.2: A crystal modelled as a lattice of atoms in harmonic potentials.

energy of each individual oscillator is

$$\varepsilon = \frac{1}{2}\kappa x^2 + \frac{1}{2}mv^2.$$

Therefore in three dimensions the system has $3 \cdot 2 \cdot N$ quadratic degrees of freedom (3 dimensions, potential and kinetic contributions, N particles). The equipartition theorem states that each quadratic degree of freedom contributes $k_B T/2$ to the mean energy so the mean energy of the system is

$$\overline{E} = 6N \frac{1}{2} k_B T = 3N k_B T.$$

The heat capacity is then

$$C_V = \frac{\partial \overline{E}}{\partial T} = 3N k_B.$$

This is known as the Dulong–Petit law which states that C_V is constant. However some substances, for example diamond, have much lower heat capacities than the Dulong–Petit law predicts. Experimental evidence also shows that C_V goes to zero as T goes to zero. The reason for these violations of the Dulong–Petit law is because energy is quantised so at low energies it is possible to increase temperature without moving up an energy level and therefore $dE/dT = 0$. The reason that this violation was noticed in diamond is because diamond is very hard which translates to diamond having a high spring constant, κ . Since quantum effects are most prevalent when $\varepsilon \sim k_B T$ a higher value of κ makes these effects more noticeable.

27.2 The Einstein Model of a Crystal

The Einstein model of a crystal is a lot like the classical model but the oscillators are replaced with quantum harmonic oscillators. Recall that a quantum harmonic oscillator in one dimension has energy

$$\varepsilon_n = \left(n + \frac{1}{2}\right) \hbar\omega.$$

Notice that this is now quantised giving discrete energy levels, ε_n for $n \in \mathbb{N} = \{0, 1, 2, \dots\}$. Another important thing is that $\varepsilon_0 = \hbar\omega/2 \neq 0$. The three dimensional harmonic oscillator is simply three linearly independent one dimensional oscillators. Its energy levels are given by

$$\varepsilon_n^{3D} = \left(n_x + n_y + n_z + \frac{3}{2}\right) \hbar\omega = \left(n + \frac{3}{2}\right) \hbar\omega.$$

This assumes an isotropic harmonic oscillator (ω the same in all directions) which fits experimental evidence.

We are considering a weakly interacting system so the partition function is

$$Z = [Z(1)]^N$$

where $Z(1)$ is the partition function for a single particle. Since the energy of the three dimensional oscillator is simply the sum of the three one dimensional oscillators there is a similar factorisation leading to

$$Z(1) = [Z^{1D}(1)]^3$$

where $Z^{1D}(1)$ is the partition function for a single particle in one dimension. Hence the partition function for the entire system is

$$Z = [Z^{1D}(1)]^{3N}.$$

The partition function for a single particle in one dimensions is

$$Z^{1D}(1) = \sum_{n=0}^{\infty} \exp \left[- \left(n + \frac{1}{2} \right) \beta \hbar \omega \right].$$

To evaluate this simply recall the formula for the sum of an infinite geometric series (see appendix D):

$$\sum_{n=0}^{\infty} a^n = \frac{1}{1-a}.$$

Identifying $a = e^{-x/2}$ where $x = \beta \hbar \omega$ we see that

$$\begin{aligned} Z^{1D}(1) &= \sum_{n=0}^{\infty} \exp \left[-\frac{x}{2} + nx \right] \\ &= e^{-x/2} \sum_{n=0}^{\infty} e^{-nx} \\ &= \frac{e^{-x/2}}{1 - e^{-x}}. \end{aligned}$$

The mean energy is then

$$\bar{E} = 3N\bar{\varepsilon} = 3N\hbar\omega \left(\bar{n} + \frac{1}{2} \right).$$

It is actually easier to calculate $\bar{\varepsilon}$ than \bar{n} since we already have a relation for the mean energy:

$$\begin{aligned} \bar{\varepsilon} &= -\frac{\partial}{\partial \beta} \ln[Z^{1D}(1)] \\ &= -\frac{\partial x}{\partial \beta} \frac{\partial}{\partial x} \ln[Z^{1D}(1)] \\ &= -\hbar\omega \frac{\partial}{\partial x} \left[-\ln(1 - e^{-x}) - \frac{1}{2} \right] \end{aligned}$$

$$= \hbar\omega \left[\frac{e^{-x}}{1 - e^{-x}} + \frac{1}{2} \right].$$

From this we see that

$$\bar{n} = \frac{e^{-x}}{1 - e^{-x}} = \frac{1}{e^x - 1}.$$

We can also calculate \bar{n} from the Boltzmann distribution:

$$\begin{aligned} \bar{n} &= \sum_{n=0}^{\infty} n P_n \\ &= \frac{1}{Z^{1D}(1)} \sum_{n=0}^{\infty} n \exp \left[-x \left(n + \frac{1}{2} \right) \right] \end{aligned}$$

using our favourite trick of differentiating under the sum we have

$$\begin{aligned} \sum_{n=0}^{\infty} n a^n &= a \frac{d}{da} \sum_{n=0}^{\infty} a^n \\ &= a \frac{d}{da} \frac{1}{1 - a} \\ &= \frac{a}{(1 - a)^2}. \end{aligned}$$

So \bar{n} is given by

$$\begin{aligned} \bar{n} &= \frac{1}{Z^{1D}(1)} \sum_{n=0}^{\infty} n \exp \left[-x \left(n + \frac{1}{2} \right) \right] \\ &= \frac{1}{Z^{1D}(1)} e^{-x/2} \sum_{n=0}^{\infty} n e^{-nx} \\ &= \frac{1}{Z^{1D}(1)} e^{-x/2} \frac{e^{-x}}{(1 - e^{-x})^2} \\ &= \frac{1 - e^{-x}}{e^{-x/2}} e^{-x/2} \frac{e^{-x}}{(1 - e^{-x})^2} \\ &= \frac{e^{-x}}{1 - e^{-x}} \\ &= \frac{1}{e^x - 1}. \end{aligned}$$

The mean total energy is then given by

$$\bar{E} = 3N\hbar\omega \left[\frac{e^{-x}}{1 - e^{-x}} + \frac{1}{2} \right]$$

and the heat capacity by

$$\begin{aligned} C_V &= \left(\frac{\partial \bar{E}}{\partial T} \right)_V \\ &= \left(\frac{\partial x}{\partial T} \right)_\omega \left(\frac{\partial \bar{E}}{\partial x} \right)_\omega \\ &= -\frac{\hbar\omega}{k_B T^2} \left(\frac{\partial \bar{E}}{\partial T} \right)_\omega \\ &= 3Nk_B \frac{x^2 e^x}{(e^x - 1)^2}. \end{aligned}$$

Notice that constant volume, V , translates to constant ω as this is the only way that volume, or variable other than temperature, can enter the model.

27.2.1 High and Low Temperature Behaviour

As with any new model one of the first things we will consider is the limiting behaviour of the system. First consider $T \rightarrow \infty$. As this happens $k_B T \gg \hbar \omega$ and so quantisation effects are negligible and we expect that the Einstein model reduces to the Dulong–Petit model (constant heat capacity). We have $x \rightarrow 0$ as $T \rightarrow \infty$ so

$$C_V \approx 3Nk_B \frac{x^2 \cdot 1}{(1 + x + \dots - 1)^2} \approx 3Nk_B \frac{x^2}{x^2} = 3Nk_B.$$

So we do indeed recover the Dulong–Petit law.

As $T \rightarrow 0$ we expect $C_V \rightarrow 0$. In this case $x \rightarrow \infty$ meaning that $e^x - 1 \approx e^x$ and so

$$C_V \approx 3Nk_B \frac{x^2 e^x}{e^{2x}} = x^2 e^{-x} \rightarrow 0.$$

So this has the expected low temperature behaviour. *However* experimental evidence shows that $C_V \sim T^3$ for low temperatures which doesn't match the Einstein model. A better model, called the Debye model, can explain this but we won't look at this model until next years condensed matter course.

28 Ideal Quantum Gas

A classical ideal gas has distinguishable particles. This is because we could pick a particle and track its path through space. A quantum ideal gas has indistinguishable particles as the uncertainty principle means we cannot track a given particle in this way.

Key Point 12

Identical, non-localised particles must be treated as indistinguishable.

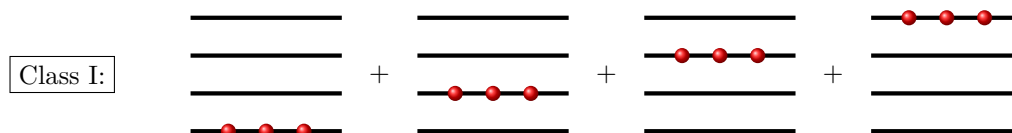
For full generality we need to consider a many-particle wave function since there aren't really any weakly interacting quantum systems. However often we can simply modify the Boltzmann distribution slightly to account for indistinguishability.

Suppose we have a system of two particles each of which can be in two different states. If this is a classical system then there are two microstates, $(a, b) = (\uparrow, \downarrow)$ and $(a, b) = (\downarrow, \uparrow)$ corresponding to both particles being in different states. In a quantum system however we can't distinguish between (a, b) and (b, a) so there is only one microstate corresponding to both particles being in different states. In general if we count microstates assuming distinguishability we will over count the number of microstates.

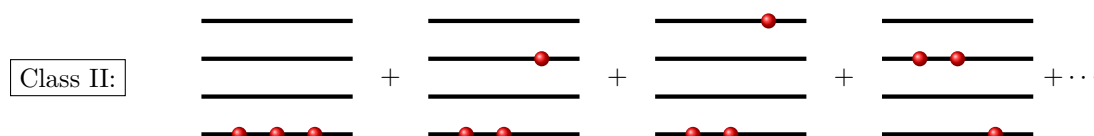
The classical partition function is

$$Z = [Z(1)]^N = \sum_{i_1, i_2, \dots, i_N} \exp[-\beta(\varepsilon_{i_1} + \varepsilon_{i_2} + \dots + \varepsilon_{i_N})].$$

We can divide this into various classes of microstate however there isn't a mathematical notation that lends itself to this so we will use diagrams. The first class of microstates is states where all particles are in the same energy level:



The next class is all but one particle in the same energy level:



And so on up to the final class which is all particles in a different energy level.

Consider a case of M energy levels. The number of microstates in class I is simply M , one for each possible energy level. The number of microstates in class II is $M(M-1)$, pick one energy level to place the lone particle and a different energy level to place the rest of the particles in. The number of microstates in the final class is $M!$. As $M \rightarrow \infty$ the final final class dominates.

If we now introduce indistinguishability we see we have over counted. Class I has no over counting. Class II will have been over counted by a factor of N as classically all particles in the lowest energy state apart from one in the second has N distinct microstates one for each particle that can be on its own. The final class will have been over counted by a factor of $N!$.

We cannot account for the different over counting of each class but since the final class dominates any sum we correct for any over counting in this term. This gives what is called the **semi-classical approximation**:

$$Z_{\text{SC}} = \frac{1}{N!} Z_{\text{classical}} = \frac{1}{N!} [Z(1)]^N.$$

28.1 Calculation of $Z(1)$

Consider a cubic box of side length L . For a free particle ($V = 0$) in this box Schrödinger's equation for is

$$\left[-\frac{\hbar^2}{2M} \nabla^2 - \varepsilon \right] \psi = 0.$$

In the one-dimensional case we have

$$\psi''(x) = -k^2 \psi, \quad \text{where} \quad k^2 = \frac{2M\varepsilon}{\hbar^2}.$$

The boundary conditions are that ψ vanishes at $x = 0, L$ and so

$$\psi(x) = A \sin(kx), \quad \text{where} \quad k = \frac{n\pi}{L}, \quad \text{for} \quad n = 1, 2, 3, \dots$$

This is a separable equation and the solution in three dimensions is simply the product of three one dimensional solutions:

$$\psi^{3D}(\mathbf{r}) = A \sin(k_x x) \sin(k_y y) \sin(k_z z), \quad \text{where} \quad k_i = \frac{n_i \pi}{L}, \quad \text{for} \quad n_i = 1, 2, 3, \dots$$

The energy is then

$$\varepsilon_n = \frac{\hbar^2}{2M} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 \pi^2}{2ML^2} (n_x^2 + n_y^2 + n_z^2).$$

To calculate the partition function we need to sum over all values n_x , n_y , and n_z :

$$Z(1) = \sum_n e^{-\varepsilon_n \beta} = \sum_{n_x, n_y, n_z} \exp \left[-\frac{\hbar^2 \pi^2}{2ML^2 k_B T} (n_x^2 + n_y^2 + n_z^2) \right].$$

This sum is not easy to compute however we can approximate it as an integral using the density of states method. This method works since the partition function depends only on the magnitude of the vector

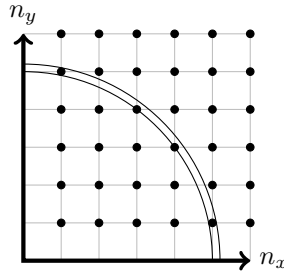


Figure 28.1: Two-dimensional \mathbf{n} space with point density 1. Shown is part of a annulus with radius n and thickness dn .

$\mathbf{n} = (n_x, n_y, n_z)$ in n -space. We want to evaluate the sum on the points with integer coordinates in

n -space. What we do is we take the fact that the density of these points is 1 per unit volume and we consider a thin spherical shell of radius n and thickness dn . The volume of this shell is $4\pi n^2 dn$ and so it contains approximately $4\pi n^2 dn$ points. However we are only interested in cases when all coordinates of \mathbf{n} are positive so this over counts by a factor of 8 meaning there are $4\pi n^2 dn/8$ points in the part of the shell in the region of interest. Using this we convert our sum into an integral. In general for some function, f , of the magnitude, n , we have

$$\sum_{n_x, n_y, n_z} f(n) \approx \frac{1}{8} \int 4\pi n^2 f(n) dn = \frac{\pi}{2} \int n^2 f(n) dn$$

where the integral is over $n \in [0, \infty)$. So the partition function is

$$\begin{aligned} Z(1) &= \sum_{n_x, n_y, n_z} \exp \left[-\frac{\hbar^2 \pi^2}{2ML^2 k_B T} (n_x^2 + n_y^2 + n_z^2) \right] \\ &\approx \frac{\pi}{2} \int n^2 \exp \left[-\frac{\hbar^2 \pi^2}{2ML^2 k_B T} n^2 \right] dn \end{aligned}$$

This approximation is good if

$$\frac{\hbar^2 \pi^2}{2ML^2} \ll k_B T.$$

We can now calculate $Z(1)$:

$$\begin{aligned} Z(1) &= \frac{\pi}{2} \int_0^\infty n^2 e^{-an^2} dn, \quad \text{where} \quad a = \frac{\hbar^2 \pi^2}{2k_B T M L^2} \\ &= \frac{1}{2} \int_{-\infty}^\infty e^{-an^2} dn \\ &= \frac{\sqrt{\pi}}{4a^{3/2}}. \end{aligned}$$

where we have used the standard result

$$\int_{-\infty}^\infty x^2 e^{-ax^2} dx = \frac{\sqrt{\pi}}{2a^{3/2}}.$$

Putting in the constants we have

$$Z(1) = \frac{\pi^{3/2}}{8} \left(\frac{2ML^2}{\beta \hbar^2 \pi^2} \right)^{3/2} = V \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2}$$

where $V = L^3$ and $h = 2\pi\hbar$.

29 Ideal Quantum Gas: Low Density Limit

29.1 Density of States

The density of states method used in the last section is very useful. It allows us to approximate a sum by an integral:

$$\sum_{n_x, n_y, n_z} A(n) \approx \frac{1}{8} \int_0^\infty A(n) 4\pi n^2 dn$$

where A is some function of n . We call $\pi^2 n^2/2$ the density of states in n -space. Recall that $k = n\pi/L$. Suppose we have some function, B , of k such that $B(k = n\pi/L) = A(n)$. We can still use the density of states method to sum B over all values of k ; we just have to do a change of variables.

$$n = \frac{L}{\pi} k \implies dn = \frac{dn}{dk} dk = \frac{L}{\pi} dk.$$

Hence

$$\sum_{n_x, n_y, n_z} \approx \int A(n) 4\pi n^2 dn$$

$$\begin{aligned}
&= \int B(k) 4\pi \frac{L^2 k^2}{\pi^2} \frac{L}{\pi} dk \\
&= \int B(k) \Gamma(k) dk
\end{aligned}$$

where

$$\Gamma(k) = \frac{k^2 V}{2\pi^2}$$

is the density of states in k -space. What this means is $\Gamma(k) dk$ is the number of states with k in $[k, k + dk]$.

Suppose now that we wish to perform a sum in energy-space. Recall that

$$\varepsilon = \frac{\hbar^2 k^2}{2M} \implies k = \sqrt{\frac{2M\varepsilon}{\hbar^2}}$$

and so

$$dk = \frac{dk}{d\varepsilon} d\varepsilon = \sqrt{\frac{2M}{\hbar^2}} \frac{1}{2\sqrt{\varepsilon}} d\varepsilon.$$

Let g denote the density of states in ε -space. Then we have

$$\Gamma(k) dk = g(\varepsilon) d\varepsilon.$$

A change of variables gives us

$$g(\varepsilon) d\varepsilon = \left(\frac{2M}{\hbar^2}\right) \frac{V}{4\pi^2} \sqrt{\varepsilon} d\varepsilon.$$

Hence the density of states in ε -space is

$$g(\varepsilon) = \left(\frac{2M}{\hbar^2}\right) \frac{V}{4\pi^2} \sqrt{\varepsilon}.$$

What this means is $g(\varepsilon) d\varepsilon$ gives the number of states with energy in $[\varepsilon, \varepsilon + d\varepsilon]$.

We can use the density of states in ε -space to calculate the partition function:

$$Z(1) = \int_0^\infty \exp(-\beta\varepsilon) g(\varepsilon) d\varepsilon.$$

Notice that $g(\varepsilon)$ increases with ε . This is because as ε increases there are more ways to distribute the energy amongst the three directions and hence more ways to have $n_x + n_y + n_z = n$ for a given value of n .

We have worked out the density of states here for a cube of volume V but it turns out that the density of states is the same for any macroscopic volume V .

29.2 Thermodynamic Variables

We now have an expression for the partition function that we can use to calculate various thermodynamic variables. The partition function is

$$Z = \frac{1}{N!} [Z(1)]^N = \frac{V^N}{N!} \left(\frac{2\pi M k_B T}{h^2} \right)^{3N/2}.$$

This allows us to calculate the free energy:

$$\begin{aligned}
F &= -k_B T \ln Z \\
&= N k_B T \left[\ln \left(\frac{1}{V} \right) - \frac{3}{2} \ln \left(\frac{2\pi M k_B T}{h^2} \right) + \ln N - 1 \right] \\
&= N k_B T \left[\ln \left(\frac{N}{V} \right) - 1 - \frac{3}{2} \ln \left(\frac{2\pi M k_B T}{h^2} \right) \right]
\end{aligned}$$

where we have used Sterling's approximation in the second line. We can also compute the average energy:

$$\begin{aligned}\bar{E} &= k_B T^2 \frac{\partial \ln Z}{\partial T} \\ &= k_B T^2 \frac{\partial}{\partial T} N \left[\ln \left(\frac{1}{V} \right) - \frac{3}{2} \ln \left(\frac{2\pi M k_B T}{h^2} \right) + \ln N - 1 \right] \\ &= \frac{3}{2} N k_B T,\end{aligned}$$

the entropy:

$$\begin{aligned}S &= \frac{\bar{E} - F}{T} \\ &= N k_B \ln \left[\left(\frac{V}{N} \right) \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \right] + \frac{5}{2} N k_B,\end{aligned}$$

the pressure:

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{N k_B T}{V} = \frac{n R T}{V},$$

which is just the ideal gas law, and the heat capacity:

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{3 N k_B}{2}.$$

We see that the ideal gas law and equipartition of energy are recovered. The recovery of the ideal gas law identifies our statistical mechanics definition of temperature ($1/T = \partial_E S$) with the thermodynamic temperature.

29.3 Entropy

Notice that the entropy in the last section takes the form $S(N, V) = N s(N/V)$ for some function s . This means that after we take out a factor of N the only N dependence is through the density, N/V . This means that entropy is additive and an extensive quantity, i.e. it scales with N .

The entropy is given by a logarithm (plus a constant that we'll ignore here) and the argument of said logarithm can be less than 1. This means that the entropy can become arbitrarily negative. This is a problem as our statistical mechanics definition of entropy doesn't allow for negative entropy as $\Omega \geq 1$ so $S = k_B \ln \Omega \geq 0$. The entropy becomes negative when, ignoring the constant term, we have

$$\frac{V}{N} \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \lesssim 1$$

or

$$\left(\frac{V}{N} \right)^{1/3} \lesssim \frac{h}{\sqrt{2\pi M k_B T}} \quad (29.1)$$

So why does the theory break down at this point? Recall that the average kinetic energy of a particle is $E_{KE} \sim 3k_B T/2$ and the typical momentum is then $p = \sqrt{2M E_{KE}} = \sqrt{3M k_B T}$. Recall also that the de Broglie wavelength is

$$\lambda_{dB} = \frac{h}{p} = \frac{h}{\sqrt{3m k_B T}}.$$

So we can identify the right hand side of 29.1 as being the typical de Broglie wavelength of a molecule of our gas. The left hand side of this equation can be interpreted as the average spacing between molecules, d , since V/N is the volume per molecule. Hence the semi-classical ideal gas model breaks down when the distance between molecules is on the same scale as the de Broglie wavelength. This is common in quantum mechanics. If we have a length scale, such as λ_{dB} , then often a classical or semi-classical approximation will break down at or below this length scale.

We call the region where the semi-classical approximation is valid the **low density limit** where the particles are spaced out enough that $d > \lambda_{dB}$. The region where the model breaks down is called the

high density limit and is when $d < \lambda_{dB}$. This region requires a full quantum treatment considering the wave function of a many particle system.

There is an alternative way that we can come to the same conclusion about where the semi-classical approximation is valid. Remember that for the semi-classical approximation we assumed that most microstates had at most one particle in a given energy level. We can find the average number of particles, \bar{n}_i , in a given quantum state, i , which, assuming distinguishable particles, is given by

$$\bar{n}_i = \frac{N \exp(-\varepsilon_i \beta)}{Z(1)}.$$

For there to be at most one particle per energy level we expect $\bar{n}_i \ll 1$ as most energy levels will be empty. This means we need

$$\frac{N}{Z(1)} = \frac{N}{V} \left(\frac{2\pi M k_B T}{h^2} \right)^{-3/2} \ll 1. \quad (29.2)$$

Rearranging this we recover the same low density limit:

$$\left(\frac{V}{N} \right)^{1/3} > \frac{h}{\sqrt{2\pi m k_B T}}.$$

30 Classical Ideal Gas

Before we can proceed further with quantum ideal gases we need to review some key classical ideal gas ideas, such as equipartition, and the Maxwell–Boltzmann distribution.

30.1 Classical Statistical Mechanics

When we use the density of states methods we take a discrete system and we approximate it as continuous. This is classical statistical mechanics as we neglect the idea of discrete states. Classical statistical mechanics is an entire field that we haven't got time to go into so we will just cover the key idea for us which is the idea of phase space. Classically a particle of an ideal gas is a member of a weakly interacting system and therefore its properties are entirely specified by its position, \mathbf{x} , and its momentum, \mathbf{p} ²⁰. This means in three dimensions that each particle has 6 degrees of freedom, $\{x, y, z, p_x, p_y, p_z\}$. We can think of each particle as corresponding to a point in six-dimensional space known as **phase space** by identifying \mathbb{R}^6 with vectors of the form $(x, y, z, p_x, p_y, p_z)^\top$. Calculations, such as calculating the partition function, then become integrals over phase space.

In classical statistical mechanics we assume particles are distinguishable and therefore we can use $Z = [Z(1)]^n$. The simplest example of a phase space calculation may be simply calculating the probability that a particle's position and momentum are in a given range. By definition

$$P(\mathbf{x}, \mathbf{p}) d^3x d^3p$$

gives the probability that a particle has position $x_i \in [x, x + dx]$ and momentum $p_i \in [p, p + dp]$. Using the Boltzmann distribution this becomes

$$\frac{1}{Z(1)} \exp[-\beta \varepsilon(\mathbf{x}, \mathbf{p})] d^3x d^3p.$$

For example if we want to know what the probability is that the particle is in space somewhere between $x = 1$ and $x = 2$ then this is given by

$$\int_1^2 dx \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \frac{1}{Z(1)} \exp[-\beta \varepsilon(\mathbf{x}, \mathbf{p})].$$

30.2 Equipartition

We have already used the equipartition theorem which states

²⁰these are conjugate variables in the sense of Hamiltonian dynamics.

Theorem: Equipartition Theorem

If a system that can be adequately described by classical statistical mechanics has a degree of freedom which contributes to the classical energy, ε , in a quadratic way then the mean contribution to the energy due to this degree of freedom is

$$\frac{1}{2}k_B T.$$

For example the classical harmonic oscillator in one dimension has energy

$$\varepsilon = \frac{p^2}{2m} + \frac{1}{2}kx^2.$$

Hence the mean energy is

$$\bar{\varepsilon} = \frac{1}{2}k_B T + \frac{1}{2}k_B T = k_B T.$$

A free particle in three dimensions has energy

$$\varepsilon = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

and hence the mean energy of this particle is

$$\bar{\varepsilon} = \frac{3}{2}k_B T.$$

The ‘proof’ of the equipartition theorem is fairly simple. Suppose that z is a degree of freedom of a system and contributes to the energy in a way that allows us to write

$$\varepsilon(z, \{\alpha\}) = az^2 + \varepsilon(\{\alpha\})$$

where $\{\alpha\}$ are all other degrees of freedom and a is a constant. Then

$$\begin{aligned} \overline{az^2} &= \frac{\int az^2 e^{-\beta\varepsilon} dz d^n\alpha}{\int e^{-\beta\varepsilon} dz d^n\alpha} \\ &= \frac{\int az^2 e^{-\beta az^2} dz}{\int e^{-\beta az^2} dz} \frac{\int e^{-\beta\varepsilon(\{\alpha\})} d^n\alpha}{\int e^{0\beta\varepsilon(\alpha)} d^n\alpha} \\ &= \frac{\int az^2 e^{-\beta az^2} dz}{\int e^{-\beta az^2} dz} \\ &= k_B T \frac{\int q^2 e^{-\beta q^2} dq}{\int e^{-\beta q^2} dq} \end{aligned}$$

where we have made the substitution $q = \beta az^2$. Now consider two cases, first suppose that z can take any real value. Then we have

$$\overline{az^2} = k_B T \frac{\int_{-\infty}^{\infty} q^2 e^{-\beta q^2} dq}{\int_{-\infty}^{\infty} e^{-\beta q^2} dq} = \frac{\sqrt{\pi}/2}{\sqrt{\pi}} = \frac{1}{2}k_B T.$$

If instead z is non-negative then we have

$$\overline{az^2} = k_B T \frac{\int_0^{\infty} q^2 e^{-\beta q^2} dq}{\int_0^{\infty} e^{-\beta q^2} dq} = \frac{\sqrt{\pi}/4}{\sqrt{\pi}/2} = \frac{1}{2}k_B T.$$

Note that if z is bound to some other range of values then equipartition may not be valid. Also equipartition is only valid at equilibrium as we used Boltzmann statistics to derive it which only apply at equilibrium.

30.3 Maxwell–Boltzmann Distribution

The Maxwell–Boltzmann distribution was originally derived by Maxwell before Boltzmann came up with his statistics. It can now be seen as a special case of the Boltzmann distribution. The Maxwell–Boltzmann distribution is the probability distribution describing the velocity distribution of a gas.

We start with the probability distribution, $P(\varepsilon)$, in energy space. We want to turn this into a probability distribution in velocity space, $P(v)$. The starting distribution is

$$P(\varepsilon) = \frac{\exp\left(-\frac{p^2}{2m}\beta\right)}{Z(1)}.$$

We are looking to find $P(v)$ such that $P(v) dv$ gives the probability that the speed of the particle is in $[v, v + dv]$. Currently we know that $P(\mathbf{p}) d^3p$ gives the probability of the momentum of the particle being in $[p_i, p_i + dp_i]$. Since a particle must have some momentum the following integral over all of momentum space must give 1:

$$1 = \int P(\mathbf{p}) d^3p.$$

This means that

$$1 = \frac{1}{Z(1)} \int \exp\left(-\frac{p^2}{2m}\beta\right) d^3p.$$

We now change to spherical coordinates in momentum space. Since an ideal gas is isotropic we can perform the angular integral and we have $d^3p = 4\pi p^2 dp$ so

$$1 = \frac{1}{Z(1)} \int_0^\infty 4\pi p^2 \exp\left(-\frac{p^2}{2m}\beta\right) dp.$$

Now making a change of variables we have $p = mv$ and hence $dp = m dv$ giving us

$$1 = \frac{1}{Z(1)} \int_0^\infty 4\pi m^2 v^2 \exp\left(-\frac{mv^2}{2}\beta\right) dv.$$

Looking at this we identify

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

This is the Maxwell–Boltzmann distribution. It increases as $\sim v^2$ for small velocities and decays away as $\sim e^{-v^2}$ for larger velocities. It allows for infinite velocities but with an incredibly small chance of that ever happening.

There are a variety of ways to interpret the ‘average’ velocity from this distribution. The first is the most probable velocity which is given by the velocity at the peak of the distribution. To find this we find v_{mp} such that $P'(v_{\text{mp}}) = 0$. If we do this we find

$$v_{\text{mp}} = \sqrt{\frac{2k_B T}{m}}.$$

The next is the mean velocity given by

$$\bar{v} = \int_0^\infty v P(v) dv = \sqrt{\frac{8k_B T}{\pi m}}.$$

Finally the root-mean-squared velocity is given by

$$\sqrt{\overline{v^2}} = \sqrt{\int_0^\infty v^2 P(v) dv} = \sqrt{\frac{3k_B T}{m}}.$$

Alternatively

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$$

by the equipartition theorem and rearranging this gives the same result. Notice that all three measures of average velocity are proportional to $\sqrt{k_B T/m}$. It doesn’t really matter which one we pick and we choose whichever better suits our needs.

31 Grand Canonical Ensembles

So far we have considered micro-canonical systems, where both energy and the number of particles are fixed, and canonical systems, where the energy is fixed. We saw that for a micro-canonical system the physics is determined by maximising the entropy whereas for a canonical system it is determined by minimising the free energy. We can view a canonical ensemble as a partition of a micro-canonical ensemble into the system and the bath. We will proceed similarly in this section to derive results for a grand canonical system but first we consider a simpler system.

31.1 Chemical Potential

Consider a canonical ensemble divided into two parts such that one part has N_1 particles and the other has N_2 . The total number of particles is simply $N = N_1 + N_2$. The free energy of the system is $F(N) = F_1(N_1) + F_2(N_2)$ where $F_i(N_i)$ are the free energies of each part. Since N is fixed if $N_1 \rightarrow N_1 + dN_1$ we must have $N_2 \rightarrow N_2 + dN_2 = N_2 - dN_1$. Hence

$$dF = \frac{\partial F_1}{\partial N_1} dN_1 + \frac{\partial F_2}{\partial N_2} dN_2 = \left[\frac{\partial F_1}{\partial N_1} - \frac{\partial F_2}{\partial N_2} \right] dN_1.$$

At equilibrium the free energy is minimised and so $dF = 0$ meaning

$$\frac{\partial F_1}{\partial N_1} = \frac{\partial F_2}{\partial N_2}.$$

We define the **chemical potential**

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}. \quad (31.1)$$

At equilibrium all subsystems must have the same chemical potential.

Out of equilibrium if the chemical potential of part i is μ_i then we have

$$dF = (\mu_1 - \mu_2) dN_1.$$

Out of equilibrium the system acts to minimise F and therefore $dF < 0$. Suppose $\mu_1 > \mu_2$; then we must have $dN_1 < 0$ so that dF is negative. Similarly if $\mu_1 < \mu_2$ then $dN_1 > 0$. We see that in a way μ controls the flow of particles between subsystems.

We can make an analogy between the chemical potential and the temperature. We know that if there is a temperature gradient then energy will flow along this gradient until equilibrium is achieved. Similarly if there is a chemical potential gradient then particles will flow along this gradient until equilibrium is achieved. The temperature plays a key role in the Boltzmann factor as a constant value. We will see that for a grand canonical system μ plays a similar role.

We can come up with a similar definition of the chemical potential based upon a micro-canonical. Split the micro-canonical ensemble into two parts in a similar way to the canonical ensemble at the start of this section. We now also have that the energy of each part is E_i and the total energy, $E = E_1 + E_2$, is fixed. The entropy of the system is

$$S(E, N) = S_1(E_1, N_1) + S_2(E_2, N_2)$$

and so similar logic to above means that we have

$$dS = \left[\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right] dE_1 + \left[\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} \right] dN_1.$$

At equilibrium S is maximised for a micro-canonical ensemble and so $dS = 0$. Since dE_1 and dN_1 are independent this means that both terms in dS above must be zero. We have already seen that

$$\left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T}.$$

Inverting the definition of the free energy we have

$$S = \frac{E - F}{T}.$$

Hence

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

Rearranging this we have

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

Example 31.1. Consider a system of an ideal gas contained in two connected volumes one of which is a height H above the other. Suppose also that the height of each volume is negligible compared to H . Let N_u be the number of particles in the upper volume and N_l be the number of particles in the lower volume. Similarly let Z_u and Z_l be the partition functions of the upper and lower volumes respectively. In the semi-classical approximation we have

$$\begin{aligned} Z(N_l, N_u) &= Z_l(N_l) Z_u(N_u) \\ &= \left[\frac{(V/\lambda^3)^{N_l}}{N_l!} \right] \left[\frac{(V/\lambda^3)^{N_u} \exp(-\beta mgHN_u)}{N_u!} \right] \end{aligned}$$

where

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}.$$

Hence the free energy of each volume is

$$\begin{aligned} F_l &= -k_B T \ln Z_l \\ &= N_l k_B T \left[\ln \left(\frac{N_l \lambda^3}{V} - 1 \right) \right], \\ F_u &= N_u k_B T \left[\ln \left(\frac{N_u \lambda^3}{V} - 1 \right) \right] + N_u mgH. \end{aligned}$$

The chemical potentials are then

$$\begin{aligned} \mu_l &= \frac{\partial F_l}{\partial N_l} = k_B T \ln \left(\frac{N_l}{V} \lambda^3 \right), \\ \mu_u &= \frac{\partial F_u}{\partial N_u} = k_B T \ln \left(\frac{N_u}{V} \lambda^3 \right) + mgH. \end{aligned}$$

So at equilibrium when we have $\mu_u = \mu_l$ we have

$$k_B T \ln \left(\frac{N_l}{N_u} \right) = mgH \implies N_u = N_l \exp \left(-\frac{mgH}{k_B T} \right).$$

So we expect more particles in the lower volume than the upper volume. Notice that both chemical potentials increases with density so the denser the gas the more pronounced the effect is. Similarly the larger H is the more difference there is between N_l and N_u .

31.2 Grand Canonical Distribution

The goal of this section is to find a statistical distribution like the Boltzmann distribution for the canonical system derived in section 23.3. The derivation is very similar so it is worth recapping that section before reading this.

Consider a micro-canonical system split into two parts which we call the system and the bath. The system has N particles and energy E , both of which can vary. The bath has energy E_b and N_b particles. The energy of the entire system is then $E_{\text{tot}} = E + E_b$ and the total number of particles is $N_{\text{tot}} = N + N_b$. The bath is considerably larger than the system and so acts as a reservoir of both energy and particles at constant temperature, T , and chemical potential, μ .

A microstate, i , of the system with energy E_i and N_i particles has probability

$$P(E_i, N_i) = \frac{\Omega(E_i, N_i)\Omega_b(E_b, N_b)}{\Omega_{\text{universe}}(E_{\text{tot}}, N_{\text{tot}})}.$$

The denominator is a constant as both E_{tot} and N_{tot} are constant so we can discard it and simply normalise at the end. The term $\Omega(E, N)$ is one since we are counting the number of microstates and there is only one microstate with energy E and N particles. Hence

$$P(E_i, N_i) \propto \Omega_b(E_{\text{tot}} - E, N_{\text{tot}} - N).$$

From the definition of entropy we can write this as

$$P(E_i, N_i) \propto \exp \left[\frac{1}{k_B} S_b(E_{\text{tot}} - E, N_{\text{tot}} - N) \right].$$

Since we assume that the entire set up is much larger than the system we have $E_{\text{tot}} \gg E$ and $N_{\text{tot}} \gg N$. This allows us to Taylor expand giving

$$S_b(E_{\text{tot}} - E, N_{\text{tot}} - N) = S_b(E_{\text{tot}}, N_{\text{tot}}) + \left. \frac{\partial S_b}{\partial E} \right|_{E=E_{\text{tot}}} (-E) + \left. \frac{\partial S_b}{\partial N} \right|_{N=N_{\text{tot}}} (-N) = \text{const} - \frac{E}{T} + \frac{N\mu}{T}.$$

Hence

$$P(E_i, N_i) \propto \exp \left[\frac{N\mu - E}{k_B T} \right].$$

This, when normalised, gives us the **grand canonical distribution**, also called the Gibbs–Boltzmann distribution.

Key Point 13

The probability that a system in equilibrium with a reservoir of energy and particles at temperature T and chemical potential μ is in the microstate i with energy E_i and particle number N_i is

$$P(E_i, N_i) = \frac{1}{\mathcal{Z}} \exp[-\beta(E_i - \mu N_i)]$$

where \mathcal{Z} is the grand canonical partition function given by

$$\mathcal{Z} = \sum_j \exp[-\beta(E_j - \mu N_j)]$$

and

$$\beta = \frac{1}{k_B T}.$$

There are two main uses of the grand canonical ensemble. The first is rather obvious, there are systems where the number of particles isn't fixed. The second is more interesting. In a similar way to how the energy of a large canonical system isn't constant but fluctuates a small amount about \bar{E} the number of particles of a large grand canonical system isn't constant but fluctuates about \bar{N} . This allows us to study canonical ensembles with N_c particles ensembles by studying grand canonical ensembles with $\bar{N} = N_c$ particles. This is useful as the restriction to have N be constant actually makes some of the mathematics harder.

For example we had to partition the energy of the system into different energy levels while keeping N fixed. This is equivalent to an open problem in number theory about partitioning integers as the sum of strictly positive integers. It is not known in general how many ways this can be done for a given integer which makes our sums very hard to do. If instead we allow a slight change in N the system is almost identical and the mathematics becomes a lot easier.

32 Quantum Gas

Recall that the grand canonical distribution for a microstate, r , with energy E_r and N_r particles is

$$P(E_r, N_r) = \frac{1}{\mathcal{Z}} \exp[-\beta(E_r - \mu N_r)], \quad \text{where} \quad \mathcal{Z} = \sum_r \exp[-\beta(E_r - \mu N_r)].$$

The mean number of particles is fairly easy to compute:

$$\begin{aligned}
\bar{N} &= \sum_r N_r P(E_r, N_r) \\
&= \frac{1}{\mathcal{Z}} \sum_r N_r \exp[-\beta(E_r - \mu N_r)] \\
&= \frac{1}{\mathcal{Z}} \sum_r \frac{1}{\beta} \frac{\partial}{\partial \mu} \exp[-\beta(E_r - \mu N_r)] \\
&= \frac{1}{\mathcal{Z}} \frac{1}{\beta} \frac{\partial}{\partial \mu} \sum_r \exp[-\beta(E_r - \mu N_r)] \\
&= \frac{1}{\mathcal{Z}} \frac{1}{\beta} \frac{\partial}{\partial \mu} \mathcal{Z} \\
&= \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z} \\
&= k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z}.
\end{aligned}$$

Here we have used

$$\frac{1}{y} \frac{\partial y}{\partial x} = \frac{\partial}{\partial x} \ln y.$$

Compare this to

$$\bar{E} = k_B T^2 \frac{\partial}{\partial \beta} \ln \mathcal{Z}$$

for a canonical system and we see that the analogy of μ being like temperature continues. Further we can show that

$$\frac{\sqrt{\Delta N^2}}{\bar{N}} \sim \frac{1}{\sqrt{\bar{N}}}.$$

This means that for large N the number of particles is sharply spiked at \bar{N} . This allows us to approximate a canonical system dependent on T as a grand canonical system dependent on T and μ by choosing μ to give \bar{N} the value of N in the canonical system.

32.1 Indistinguishable Particles

For distinguishable particles to have complete information about a system we need to know exactly which state each particle is in. For indistinguishable particles we need to know only how many particles are in each state as it doesn't matter which particle we consider as they are all the same.

Key Point 14

A microstate for distinguishable particles is specified by the state, i_j , of each particle where i_j represents the j th particle being in state i .

A microstate for indistinguishable particles is specified by occupation number, n_i , of the i th state.

For a given microstate of a system of indistinguishable particles it is then quite simple to compute N_r , the total number of particles in the microstate, it is simply the number of particles in each state summed over each state:

$$N_r = \sum_i n_i.$$

Similarly the energy of the microstate, E_r , is just the sum of the energies of each state:

$$E_r = \sum_i n_i \varepsilon_i$$

where ε_i is the energy of the i th state.

This allows us to rewrite the exponent of the Boltzmann–Gibbs factor as

$$-\beta(E_r - \mu N_r) = -\beta \sum_i n_i (\varepsilon_i - \mu).$$

Similarly a sum over all microstates becomes a series of sums over each quantum state (i.e. the state of a single particle):

$$\sum_r \rightarrow \sum_{n_1} \sum_{n_2} \cdots$$

We saw this previously with a canonical ensemble and this sum was very hard to do as we had to keep N fixed. This meant that, for example, the value of n_1 effected the allowed values of n_2 . In a grand canonical ensemble we don't have this restriction and the sums decouple.

The partition function can be written as

$$\begin{aligned} \mathcal{Z} &= \sum_r \exp[-\beta(E_r - \mu N_r)] \\ &= \sum_{n_1} \sum_{n_2} \cdots \sum_{n_j} \exp \left[-\beta \sum_i n_i (\varepsilon_i - \mu) \right] \\ &= \left[\sum_{n_1} \exp[-\beta n_1 (\varepsilon_1 - \mu)] \right] \left[\sum_{n_2} \exp[-\beta n_2 (\varepsilon_2 - \mu)] \right] \cdots \left[\sum_{n_j} \exp[-\beta n_j (\varepsilon_j - \mu)] \right] \\ &= \mathcal{Z}_1 \mathcal{Z}_2 \cdots \mathcal{Z}_j \\ &= \prod_i \mathcal{Z}_i \end{aligned}$$

where \mathcal{Z}_i is the partition function for the quantum state i . We see that the partition function factors into single state partition functions. Compare this to the partition function for a canonical distribution which factors into single particle partition functions.

We can then perform the usual sorts of calculations using this factorisation. For example the probability of being in a microstate r with corresponding occupancies $\{n_1, n_2, \dots\}$ is given by

$$\begin{aligned} P(N_r, E_r) &= P(n_1, n_2, \dots) \\ &= \frac{\exp[-\beta n_1 (\varepsilon_1 - \mu)]}{\mathcal{Z}_1} \frac{\exp[-\beta n_2 (\varepsilon_2 - \mu)]}{\mathcal{Z}_2} \cdots \\ &= P(n_1) P(n_2) \cdots \end{aligned}$$

where $P(n_i)$ is the probability that state i has n_i particles:

$$P(n_i) = \frac{\exp[-\beta n_i (\varepsilon_i - \mu)]}{\mathcal{Z}_i}.$$

32.2 Fermions and Bosons

For the first time in statistical mechanics we now need to actually consider what the particles are. There are two possible cases:

- **Fermions** have half integer spin (i.e. $s = \hbar(2n + 1)/2$). Common examples include electrons, protons, neutrons, and ^3He .
- **Bosons** have integer spin (i.e. $s = \hbar n/2$). Common examples include photons, the Higg's boson, and ^4He .

The key difference for our purposes is the Pauli exclusion principle which states that there can only be at most one fermion in a given quantum state. This means that if our particles are fermions then n_i can only take the values 0 or 1. The quantum state partition function for a fermionic system is

$$\mathcal{Z}_i = \sum_{n_i=0,1} \exp[-\beta n_i (\varepsilon_i - \mu)] = 1 + \exp[-\beta (\varepsilon_i - \mu)].$$

Conversely there is no restriction on the number of bosons in a given state so the most general case is

$$\mathcal{Z}_i = \sum_{n_i=0}^{\infty} \exp[-\beta n_i (\varepsilon_i - \mu)]$$

$$\begin{aligned}
&= \sum_{n_i=0}^{\infty} \exp[-\beta(\varepsilon_i - \mu)]^{n_i} \\
&= \frac{1}{1 - \exp[-\beta(\varepsilon_i - \mu)]}
\end{aligned}$$

which holds only if $|\exp[-\beta(\varepsilon_i - \mu)]| < 1$ as we have used the result for a geometric series that

$$\sum_{n=0}^{\infty} a^n = \frac{1}{1-a}$$

for $|a| < 1$ (see appendix D).

We can now calculate \bar{n}_i , the average number of particles in quantum state i . We can do the derivation for both fermions and bosons at the same time by noting that

$$\mathcal{Z}_i = [1 \pm \exp(-\beta[\varepsilon_i - \mu])]^{\pm 1}$$

where we take $+$ for fermions and $-$ for bosons. The average occupancy is

$$\bar{n}_i = \sum_{n_i} n_i P(n_i) = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z}_i.$$

We showed this earlier for \bar{N} but it is the same if we consider only a single state. Hence

$$\begin{aligned}
\bar{n}_i &= \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln[(1 \pm \exp(-\beta(\varepsilon_i - \mu)))^{\pm 1}] \\
&= \pm \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln[1 \pm \exp(-\beta(\varepsilon_i - \mu))] \\
&= \pm \frac{1}{\beta} \frac{(\pm \beta) \exp[-\beta(\varepsilon_i - \mu)]}{1 \pm \exp[-\beta(\varepsilon_i - \mu)]} \\
&= \frac{\exp[-\beta(\varepsilon_i - \mu)]}{1 \pm \exp[-\beta(\varepsilon_i - \mu)]} \\
&= \frac{1}{\exp[\beta(\varepsilon_i - \mu)] \pm 1}
\end{aligned}$$

Key Point 15

The mean number of particles in quantum state i (which has energy ε_i) is given by:

- the Fermi–Dirac distribution for fermions:

$$\bar{n}_i = f_+(\varepsilon_i) = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] + 1}$$

- the Bose–Einstein distribution for bosons:

$$\bar{n}_i = f_-(\varepsilon_i) = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] - 1}$$

The number of particles is then determined by

$$N = \sum_i \bar{n}_i = \sum_i f_{\pm}(\varepsilon_i).$$

33 Ideal Fermi Gas

33.1 Low Density Limit

Consider the case of $\mu \ll -1$. This means that $e^{-\beta\mu} \gg 1$ and so

$$\bar{n}_i = f_{\pm}(\varepsilon_i) = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] \pm 1} \approx e^{-\beta(\varepsilon_i - \mu)}$$

for both fermions and bosons. Suppose we are interested in a canonical system with N fixed. We can model this by fixing μ such that

$$N = \sum_i \bar{n}_i \approx e^{\beta\mu} \sum_i e^{-\beta\varepsilon_i} = e^{\beta\mu} Z(1)$$

where $Z(1)$ is the usual canonical single-particle partition function. Then in the limit of large, negative μ we have

$$\mu \approx k_B T \ln \left(\frac{N}{Z(1)} \right).$$

This recovers the semi-classical approximation of μ from example 31.1. This is called the low density limit (or high temperature limit) because in this limit we have

$$\mu \ll -1 \implies \ln \left(\frac{N}{Z(1)} \right) \ll -1 \implies \frac{N}{Z(1)} \ll 1$$

which is the low density limit from equation 29.2 where the semi-classical partition function worked well.

33.2 Ideal Fermi Gas

Consider the Fermi–Dirac distribution in the limit $T \rightarrow 0$. We then have $\beta \rightarrow \infty$ and we find that

$$f_+(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1} \rightarrow \begin{cases} 1, & \text{if } \varepsilon < \varepsilon_f, \\ 0, & \text{if } \varepsilon > \varepsilon_f, \end{cases}$$

where ε_f is the **Fermi energy** defined to be

$$\varepsilon_f = \lim_{T \rightarrow 0} \mu(T).$$

The Fermi–Dirac distribution gives the average number of particles in a given state. However since these are fermions there can only be zero or one particle and so the Fermi–Dirac distribution is also the probability that a state is occupied. Therefore at $T = 0$ what we see is that all states with $\varepsilon < \varepsilon_f$ are occupied and all states with $\varepsilon > \varepsilon_f$ are unoccupied. This is shown in figure 33.1. Contrast this with a

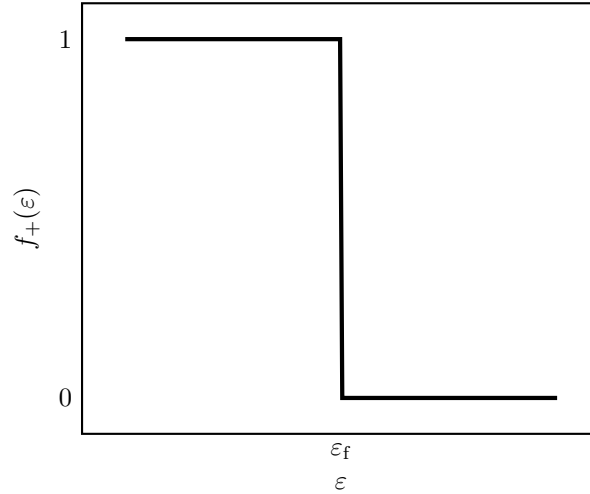


Figure 33.1: The Fermi–Dirac distribution at $T = 0$.

classical gas where at $T = 0$ all particles would be in the ground state of $\varepsilon = 0$. The Fermi energy arises naturally from the Pauli exclusion principle and the fact that energy levels ‘fill up’.

Clearly at low temperatures the Fermi energy is going to be important but what *is* the Fermi energy. To calculate this we use the density of states method in ε -space. Let g be the density of states in ε -space. Then

$$N = \sum_i f_+(\varepsilon_i) \approx \int_0^\infty g(\varepsilon) f_+(\varepsilon) d\varepsilon.$$

Recall that g is such that $g(\varepsilon) d\varepsilon$ gives the number of states with energy in $(\varepsilon, \varepsilon + d\varepsilon)$. In section 29.1 we showed that for spinless particles in a box

$$g(\varepsilon) = DV\sqrt{\varepsilon}, \quad \text{where} \quad D = \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{4\pi^2}.$$

If we now allow particles to have spin, s , then each translational state now corresponds to $2s + 1$ states and so

$$g(\varepsilon) = \tilde{D}V\sqrt{\varepsilon}, \quad \text{where} \quad \tilde{D} = (2s + 1)D.$$

At $T = 0$ we have $f_+(\varepsilon) = 0$ for $\varepsilon > \varepsilon_f$ and $f_+(\varepsilon) = 1$ for $\varepsilon < \varepsilon_f$. Hence

$$\begin{aligned} N &= \sum_i f_+(\varepsilon_i) \\ &\approx \int_0^\infty g(\varepsilon) f_+(\varepsilon) d\varepsilon \\ &= \int_0^{\varepsilon_f} g(\varepsilon) d\varepsilon \\ &= \tilde{D}V \int_0^{\varepsilon_f} \sqrt{\varepsilon} d\varepsilon \\ &= \tilde{D}V \frac{2}{3} \left[\varepsilon^{3/2} \right]_0^{\varepsilon_f} \\ &= \frac{2}{3} \tilde{D}V \varepsilon_f^{3/2}. \end{aligned}$$

Rearranging this we have

$$\varepsilon_f = \left(\frac{3N}{2\tilde{D}V} \right)^{2/3} = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{(2s + 1)V} \right)^{2/3}.$$

It can be shown that

$$E(T = 0) = \int_0^{\varepsilon_f} g(\varepsilon) \varepsilon d\varepsilon = \frac{3}{5} \varepsilon_f.$$

From this we see that the average energy per particle at $T = 0$ is

$$\frac{E}{N} = \frac{3}{5} \varepsilon_f.$$

Some points to note:

- ε_f decreases with the mass of the fermion, m .
- ε_f increases with the density, N/V .
- ε_f defines a characteristic temperature called the **Fermi temperature**, T_f which is such that $\varepsilon_f = k_B T_f$.
- At $T = 0$ each particle has non-zero energy, $\varepsilon = 3\varepsilon_f/5$.

33.3 Low Temperature Behaviour

Consider what happens now if instead of at $T = 0$ we are at some small, but non-zero, temperature? In this case we have

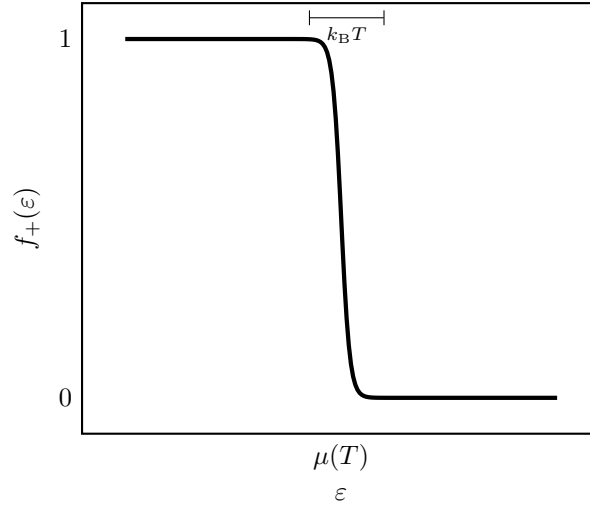
$$f_+(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1} \rightarrow \begin{cases} 1, & \text{if } \beta(\varepsilon - \mu) \ll -1, \\ 0, & \text{if } \beta(\varepsilon - \mu) \gg 1, \\ \frac{1}{2}, & \text{if } \varepsilon = \mu. \end{cases}$$

This is very similar to the result at $T = 0$ but slightly smoothed out. It differs only when $|\varepsilon - \mu| \sim \mathcal{O}(k_B T)$. For the Fermi distribution still approximate its value at $T = 0$ we must have

$$k_B T \ll \mu(T) \approx \varepsilon_f$$

or equivalently

$$T \ll T_f.$$

Figure 33.2: The Fermi–Dirac distribution for small T .

We’ve assumed that for low temperatures $\mu(T) \approx \varepsilon_f = \mu(0)$, which is the case, in fact we can show that

$$\mu(T) = \varepsilon_f \left[1 - \mathcal{O}\left(\frac{T^2}{T_f^2}\right) \right].$$

So to first order $\mu(T) = \varepsilon_f$.

We can think of the low temperature case as the zero temperature case with a small number of fermions in an excited state which leaves a small number of lower energy states unoccupied. As a rough estimate we expect that the total energy increase as the temperature increases from 0 to T will be proportional to the number of excited particles times the typical energy of an excited fermion. The fraction of excited particles is $Nk_B T / \varepsilon_f$ and the average excited energy is $k_B T$ so we expect

$$\Delta E = E(T) - E(0) \sim \frac{Nk_B T}{T} k_B T.$$

Similarly the heat capacity is

$$C_V = \frac{\partial E}{\partial T} \approx \frac{\Delta E}{\Delta T} = \frac{E(T) - E(0)}{T - 0} \sim \frac{Nk_B^2 T}{\varepsilon_f}.$$

Notice that this scales as T whereas for a classical ideal gas C_V is constant and equal to $3Nk_B T/2$.

33.4 Electron Gas

The most basic example of a Fermi gas is an electron gas. This arises mostly when we consider conduction in a metal. In a metal each atom denotes some electrons to the sea of delocalised electrons. While the atoms are held in a crystal lattice the electrons are free to move and modelling them as a gas can lead to reasonable results. Since electrons have spin $1/2$ they are fermions and so the most basic model is as an ideal Fermi gas, called a free electron gas.

For most metals $\varepsilon_f \gg k_B T$ at all reasonable operating temperatures and therefore the ideal Fermi gas approximation is valid so long as there are no other effects getting in the way.

34 Ideal Bose Gas

Recall that for bosons the average occupancy of a state with energy ε is given by the Bose–Einstein distribution:

$$\bar{n}(\varepsilon) = f_{-(\varepsilon)} = \frac{1}{\exp[\beta(\varepsilon - \mu)] - 1}.$$

The exclusion principle doesn’t apply to bosons and so the most important quantum effect is simply the indistinguishability of bosons.

34.1 Quanta as Bosons

Recall that a quantum harmonic oscillator at frequency ω has energy levels

$$\varepsilon_n = \hbar\omega \left(n + \frac{1}{2} \right).$$

In section 27.2 we showed that

$$\bar{n} = \frac{1}{e^{\beta\hbar\omega} - 1}.$$

Comparing this to the Bose–Einstein distribution we see that the Bose–Einstein distribution can be thought of as the average number of bosons in a quantum state with energy $\hbar\omega$ and chemical potential $\mu = 0$.

This suggests that we can treat quanta of energy as bosons. This idea becomes more reasonable when we consider that there is no restriction on the number of quanta and that quanta's of energy are indistinguishable. This idea becomes obvious when we identify quanta of energy as photons which are spin 0 and therefore bosons.

The fact that $\mu = 0$ means that we can add or remove quanta without violating any laws. The number of quanta is not conserved, just the total energy. Recall that in equation 31.1 we defined the chemical potential to be

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

so we see that $\mu = 0$ simply corresponds to minimising free energy with respect to the number of quanta, N .

34.2 Wave–Particle Duality

This view of quanta as bosons gives us a new way of thinking about wave–particle duality:

- Standing waves, or normal modes, of the system have discrete frequencies, ν , or angular frequencies, ω .
- From quantum mechanics we know that energy is quantised and therefore the energy in a mode is $\varepsilon = nh\nu + C$ for some constant C .
- Quanta can be treated as bosons and where the average number of bosons in a given quantum state with energy $\varepsilon = h\nu$ is given by the Bose–Einstein distribution:

$$\bar{n}(\nu) = \frac{1}{e^{\beta h\nu} - 1}.$$

This tells us how energy is distributed among the different frequencies.

We can view this as a sort of double quantisation. First start with classical one-dimensional waves satisfying

$$\frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} = \frac{\partial^2 \psi}{\partial x^2}.$$

With boundary conditions such that $\psi(0) = \psi(L) = 0$ this is solved easily by separation of variables. Simply make the ansatz that $\psi(x, t) = X(x)T(t)$ and so

$$\frac{1}{c^2} \frac{1}{T} \frac{d^2 T}{dt^2} = \frac{1}{X} \frac{d^2 X}{dx^2} = -k^2$$

where k is a constant and we choose to use $-k^2$ to make the solution nicer. From this we have

$$X(x) = \sin\left(\frac{m\pi x}{L}\right)$$

where the boundary conditions impose $k = m\pi/L$. We also have

$$\frac{1}{c^2} \frac{d^2 T}{dt^2} = -k^2 T$$

which is the normal simple harmonic oscillator with angular frequency $\omega = kc$.

Suppose we now replace the ordinary harmonic oscillator with a quantum harmonic oscillator. We know that this then has energy

$$\varepsilon_{m,n} = \hbar\omega \left(n + \frac{1}{2}\right) = \frac{\hbar m \pi c}{L} \left(n + \frac{1}{2}\right).$$

So we see that energy is twice quantised by m and n . We can view the standing waves as the states which are quantised and then the energy quanta can be viewed as bosons in these states.

34.3 Black Body Radiation

A black body is one that absorbs all radiation. This means that when it is cold it appears black. However when it is heated up a black body must emit radiation as it cannot heat up indefinitely. It is this radiation that makes black bodies interesting in physics. It seems that this radiation depends only on the temperature of the body, not what it is made of. The classical description of a black body also failed to properly account for radiation in the ultraviolet range.

An idealised black body is really quite simple. We simply take an adiabatic box at some fixed temperature, T , and cut a small hole in it. The hole must be small so that energy can be exchanged but not particles. The radiation will have the same spectrum as the radiation which is inside the cavity.

The radiation inside the cavity is simply formed of electromagnetic standing waves of frequency ν . We can treat the photons as bosons and then we find that the average energy in a mode of given frequency, ν , is

$$\bar{\varepsilon}(\nu) = \hbar\nu \bar{n}(\nu) = \frac{\hbar\nu}{e^{\beta\hbar\nu} - 1}.$$

Consider a cubic cavity with side length L . The waves must vanish at the walls so we have $2L/\lambda_x = m_x$ and similar for the other directions. Each component of the momentum is

$$p_x = \frac{h}{\lambda_x} = \frac{\hbar m_x}{2L}.$$

So the magnitude of the momentum is

$$p = \frac{\hbar}{2L} \sqrt{m_x^2 + m_y^2 + m_z^2}.$$

So we see that by restricting $m_i \in \mathbb{Z}$ we restrict the values that ν can take since $\nu = cp/h$. As usual sums are hard and integrals are (relatively) easy so we want to find a density of modes approximation. The density of modes in m -space is similar to the density of states in n -space except that there are two possible orthogonal polarisations which gives an extra factor of 2 so we have

$$\sum_{\text{modes}} A(\nu) \approx \pi \int_0^\infty A[\nu(m)] m^2 dm = \pi \int_0^\infty A(\nu) \left(\frac{2L}{c}\right)^3 \nu^2 d\nu.$$

So we can define the density of modes, g , as

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

which is such that $g(\nu) d\nu$ gives the number of modes with frequency in $[\nu, \nu + d\nu]$.

The energy contained in modes with frequency in $[\nu, \nu + d\nu]$ is then

$$\hbar\nu \bar{n}(\nu) g(\nu) d\nu = \frac{8\pi V \hbar}{c^3} \frac{\nu^3 d\nu}{e^{\beta\hbar\nu} - 1}.$$

The spatial energy density is given by

$$u(\nu) = \frac{8\pi \hbar}{c^3} \frac{\nu^3}{e^{\beta\hbar\nu} - 1}.$$

This is called the **Planck distribtuion**. It is common to write this as a function of the wavelength $\lambda = c/\nu$ which requires that we use

$$d\nu = \left| \frac{d\nu}{d\lambda} \right| d\lambda$$

which will give us

$$u(\lambda) d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{\beta hc/\lambda} - 1}.$$

Notice that the only dependence on the cavity appears as temperature (since $\beta = 1/k_B T$). There is no dependence on the shape or material of the cavity.

Consider the high temperature limit where $h\nu/k_B T \ll 1$ so $\beta h\nu \ll 1$. In this limit if we define $x = \beta h\nu$ we have

$$\begin{aligned} u(\nu) &\propto \frac{x^3}{e^x - 1} \\ &= \frac{x^3}{1 + x + \dots - 1} \\ &= \frac{x^3}{x + \dots} \\ &\approx x^2. \end{aligned}$$

If we kept track of the constants then we would find

$$u(\nu) \approx \frac{8\pi k_B T}{c^3} \nu^2.$$

Notice that this goes as ν^2 . This is a classical result as h does not appear and indeed it can be derived classically. This result leads to the ultraviolet catastrophe, since it breaks down for high ν , which was one of the clues that lead to quantum mechanics in the first place.

The correct high frequency limit when $h\nu/k_B T \gg 1$, again setting $x = \beta h\nu \gg 1$, is

$$\begin{aligned} u(\nu) &\propto \frac{x^3}{e^x - 1} \\ &\approx \frac{x^3}{e^x} \\ &= x^3 e^{-x}. \end{aligned}$$

Again if we had kept all of the constants we would have found

$$u(\nu) \approx \frac{8\pi h}{c^3} \nu^3 e^{-\beta h\nu}.$$

This decays much more rapidly and we don't have to worry about the ultraviolet catastrophe any more.

35 Radiation Gas

35.1 Stefan–Boltzmann Law

The average energy per unit volume, that is the energy density, of a cavity times the speed of light gives the energy flux through the hole in the cavity. The energy density can be calculated as

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

To evaluate this integral first let $x = \beta h\nu$ then $dx = \beta h d\nu$ and we have

$$\frac{\overline{E}}{V} = \frac{8\pi h}{c^3} \frac{1}{(\beta h)^4} \int_0^\infty \frac{x^3}{e^x - 1} dx. \quad (35.1)$$

This integral is now dimensionless and can be computed by numerical methods or it can be done analytically (see appendix E)²¹. Either way the result is $\pi^4/15$. What is actually important for us though is that the integral is just a constant and we see that $\overline{E}/V \propto T^4$. This is called the Stefan–Boltzmann law.

²¹definitely worth checking out, the zeta and gamma functions both make appearances!

35.2 Thermodynamics of Radiation Gas

Recall that in section 32.1 we say that we can factorise the partition function as

$$\mathcal{Z} = \prod_i \mathcal{Z}_i = \prod_i \frac{1}{1 - \exp[-\beta(\varepsilon_i - \mu)]}.$$

We also have $\mu = 0$ for photons. In an analogous way to ideal gases we can define the free energy as

$$\begin{aligned} F &= -k_B T \ln \mathcal{Z} \\ &= -k_B T \ln \left[\prod_i \mathcal{Z}_i \right] \\ &= -k_B T \sum_i \ln \mathcal{Z}_i \\ &= -k_B T \sum_i \ln \left[\frac{1}{1 - \exp(-\beta \varepsilon_i)} \right] \\ &= k_B T \sum_i \ln [1 - \exp(-\beta \varepsilon_i)]. \end{aligned}$$

If we then apply the density of modes approximation we have

$$\begin{aligned} F &\approx k_B T \int_0^\infty \ln[1 - e^{-\beta h \nu}] g(\nu) d\nu \\ &= \frac{8\pi k_B T}{c^3} \int_0^\infty \nu^2 \ln[1 - e^{-\beta h \nu}] d\nu. \end{aligned}$$

Similarly we can calculate the mean energy using

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}$$

and we find that

$$\bar{E} = \frac{8\pi h}{c^3} V \int_0^\infty \frac{\nu^3}{e^{\beta h \nu} - 1} d\nu$$

which is the result that we found in the previous section (equation 35.1). Using the thermodynamic relation

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

we can also define a sensible notion of pressure as

$$P = -\frac{8\pi k_B T}{c^3} \int_0^\infty \nu^2 \ln[1 - e^{-\beta h \nu}] d\nu.$$

If we integrate this by parts we find that

$$P = \frac{1}{3} \frac{\bar{E}}{V}. \quad (\text{radiation})$$

Notice that this is distinct from an ideal gas where we have

$$P = \frac{N k_B T}{V} = \frac{2}{3} \frac{\bar{E}}{V}. \quad (\text{ideal gas})$$

We can also define the compressibility,

$$K = -V \left(\frac{\partial P}{\partial V}\right)_T$$

and for radiation we have

$$K = 0. \quad (\text{radiation})$$

again contrast this with an ideal gas where

$$K = P. \quad (\text{ideal gas})$$

What this means is that an ideal gas when compressed will have a pressure increase but a photon gas can be compressed without pressure change as the number of photons is not fixed (since $\mu = 0$) and therefore compression simply decreases the number of photons so the pressure doesn't change.

We can calculate the average number of photons in a cavity:

$$\begin{aligned}\bar{N} &= \int_0^\infty \bar{n}(\nu)g(\nu) d\nu \\ &= \frac{8\pi V}{c^3} \int_0^\infty \frac{\nu^2}{1 - e^{\beta h\nu}} d\nu\end{aligned}$$

now letting $x = \beta h\nu$ we have

$$\begin{aligned}&= \frac{8\pi V}{c^3} \left(\frac{k_B T}{h}\right)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx \\ &\approx 8\pi V \left(\frac{k_B T}{ch}\right)^3 \cdot 2.404\end{aligned}$$

again see E. We find that the average energy per particle is

$$\frac{\bar{E}}{\bar{N}} \approx 2.7 k_B T \quad (\text{radiation})$$

which can be compared with the equipartition for an ideal gas with f degrees of freedom:

$$\frac{\bar{E}}{N} = \frac{f}{2} k_B T. \quad (\text{ideal gas})$$

We can also compute the heat capacity:

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{32\pi^2 k_B^4}{15c^3 h^3} T^3 V. \quad (\text{radiation})$$

Notice that this goes as T^3 this agrees with the Debye model. Compare this to an ideal gas where

$$C_V = \frac{f}{2} R \quad (\text{ideal gas})$$

which is constant.

Finally consider the entropy:

$$S = \int_0^T \frac{C_V(T')}{T'} dT' = \frac{1}{3} \frac{32\pi^5 k_B^4}{15c^3 h^3} T^3 V$$

interestingly we see that an adiabatic process for a photon gas means that $T^3 V$ must be constant. The entropy per particle is then

$$\frac{S}{\bar{N}} = 3.6 k_B T$$

35.3 Cosmic Background Radiation

Shortly after the big bang the universe was incredibly hot. At this point the universe was a hot plasma in thermal equilibrium with radiation. The universe cooled and expanded and the plasma formed atoms but the radiation remained. This radiation now forms the cosmic background radiation. Measuring this radiation and fitting the distribution to the Planck distribution we find a very good fit with temperature $T = 2.74$ K. So the radiation of the early universe has cooled down to about 3 K.

36 Bose–Einstein Condensate

Consider a Bose gas with $\mu \neq 0$. The average number of bosons is fixed and we choose μ to get the correct value of \bar{N} . The average number of particles in state with energy ε_i is

$$\bar{n}(\varepsilon_i) = f_-(\varepsilon_i) = \frac{1}{\exp[\beta(\varepsilon_i - \mu)] - 1}.$$

Using the density of states approximation we need to choose μ such that N as given by

$$N = \sum_i f_-(\varepsilon_i) \approx \int_0^\infty g(\varepsilon) \frac{1}{\exp[\beta(\varepsilon - \mu)] - 1} d\varepsilon$$

has the correct value. For spinless bosons in a box the density of states is given by $DV\sqrt{\varepsilon}$ where D is a constant and V is the volume of the box (see section 29.1). So we need to solve

$$N = DV \int_0^\infty \frac{\sqrt{\varepsilon}}{\exp[\beta(\varepsilon - \mu)] - 1} d\varepsilon$$

for μ . Recall that the average occupation number for any state must be non-negative and therefore we need to have $e^{-\beta\mu} > 1$ which means that $\mu < 0$. Let $x = \beta\varepsilon$ and therefore $dx = \beta d\varepsilon$. This substitution gives us

$$N = DV(k_B T)^{3/2} \int_0^\infty \frac{\sqrt{x}}{e^x e^{-\beta\mu} - 1} dx.$$

Assume now that we solve this for a particular temperature, T_1 , call this solution $\mu_1 = \mu(T_1)$. Now consider a second temperature, $T_2 < T_1$, and find the solution $\mu_2 = \mu(T_2)$. At this lower temperature the prefactor for the integral, $T_2^{3/2} < T_1^{3/2}$, and also $\beta_2 > \beta_1$ so for constant μ we have $e^{-\beta_2\mu} > e^{-\beta_1\mu}$. So if we want to keep N constant then we must have that μ increases (recall μ is negative so its absolute value decreases). In fact μ will increase until T reaches the **Bose temperature**, T_B , and below this temperature $\mu = 0$. At the Bose temperature we have

$$N = DV(k_B T_B)^{3/2} \int_0^\infty \frac{\sqrt{x}}{e^x - 1} dx.$$

This integral is computed in appendix E and we find it to be approximately $1.306\sqrt{\pi}$. Below T_B we cannot satisfy the equation for N to be constant. So what happens to all the bosons? The answer is they are in the ground state. This occurs due to the fact that the density of states approximation is only an approximation. This approximation works best away from the origin as over large distances in ε -space it is reasonable to treat the states as continuous. Near the origin however the density of states method doesn't account for the contribution of the state at $\varepsilon = 0$. We can fix the problem by including an extra term, \bar{n}_0 , which accounts for the mean number of particles in the ground state and so for $T < T_B$ we have

$$N = \bar{n}_0 + \int_0^\infty \frac{g(\varepsilon)}{e^{\beta\varepsilon} - 1} d\varepsilon.$$

It can be shown that

$$\bar{n}_0 = N \left[1 - \left(\frac{T}{T_B} \right)^{3/2} \right]$$

so for $T \approx T_B$ \bar{n}_0 is negligible but for $T \ll T_B$ \bar{n}_0 becomes important.

Below the Bose temperature a finite (non-zero) fraction of particles are in the ground state. We have what is called a **Bose-Einstein Condensate**. Since so many particles are in low energy states quantum mechanical effects, such as superfluidity and superconductivity, become noticeable. These effects can also occur in other materials but they are usually swamped by thermal effects however since a Bose-Einstein condensate allows for so many particles to be in a low energy state quantum effects can be seen on a macroscopic scale.

The existence of Bose-Einstein condensates follows immediately from the indistinguishability of particles. Suppose a system of indistinguishable particles are all in the ground state and that the next energy level is at $\Delta\varepsilon$. For distinguishable particles there are N ways to choose a particle to excite and the entropy gain of this excitation is thus $k_B \ln N$ which, for sufficiently large N , will win out against minimising energy when it comes to minimising the free energy. So any system of enough particles to be macroscopic will also have some excited particles.

Consider now the same system but with indistinguishable particles. Then which particle becomes excited is unimportant and the entropy change due to a single excitation will simply be $k_B \ln 1 = 0$. So energy minimising will win and the system will remain in the unexcited state. While this example of all particles in the ground state is not realistic the same logic applies if a significant number of particles are in the ground state.

36.1 Quantum Gasses Summary

The main difference between fermions and bosons lies in their behaviour at low temperatures and densities. Fermions follow the Pauli exclusion principle and therefore at low temperatures there is still energy separation between particles. We can think of this as an effective repulsion between fermions. Bosons on the other hand have no such restriction and in fact tend towards all being in the ground state as the temperature decreases which we can think of as an effective attraction between bosons.

At high temperatures but low density still the differences between fermions and bosons are less important and a more classical treatment works where we treat particles as point particles with definite position and momentum except when colliding. We can tell that the quantum nature of these particles is less important as h or \hbar appears in some formulae, such as the partition function and entropy, but vanishes in physically measurable quantities such as entropy differences.

At low temperature and high densities the quantum nature of gasses is very important, which can be seen from the emergence of \hbar in physically measurable quantities.

Appendix

A Integral of $\ln x$

The integral of the logarithm can be computed by parts. Let

$$I = \int \ln x \, dx$$

and

$$\begin{aligned} u &= \ln x, & v &= x, \\ u' &= \frac{1}{x}, & v' &= 1. \end{aligned}$$

Then

$$\begin{aligned} I &= x \ln x - \int \frac{x}{x} \, dx \\ &= x \ln x - \int 1 \, dx \\ &= x \ln x - x + C \end{aligned}$$

So

$$\int_a^b \ln x \, dx = b \ln b - b - a \ln a + a.$$

B Trapezium Rule

The trapezium rule for approximating an integral works by approximating the area under a curve with a series of trapeziums. If the trapeziums all have width Δx and we are integrating from a to b and we have $n = (b - a)/\Delta x$ trapeziums then the integral of f can be approximated as

$$\begin{aligned} \int_a^b f(x) \, dx &\approx \sum_{k=1}^n \frac{f(a + k\Delta x) - f(x + [k + 1]\Delta x)}{2} \Delta x \\ &= \frac{\Delta x}{2} [f(a) + 2f(a + \Delta x) + 2f(a + 2\Delta x) + \cdots + 2f(b - 2\Delta x) + 2f(b - \Delta x) + f(b)]. \end{aligned}$$

This can be derived by looking at the areas of the individual trapeziums, which is, for a trapezium with parallel sides of length α and β and distance between these sides of h is

$$A = \frac{\alpha}{\beta} h = \frac{f(x + k\Delta x) + f(x + [k + 1]\Delta x)}{2} \Delta x.$$

We then sum this over all trapezia giving us the trapezium rule.

C Gaussian Integrals

A Gaussian integral is one of the form

$$I = \int_{-\infty}^{\infty} e^{-\alpha x^2} \, dx.$$

These can be computed as follows:

$$\begin{aligned} I^2 &= \left[\int_{-\infty}^{\infty} e^{-\alpha x^2} \, dx \right] \left[\int_{-\infty}^{\infty} e^{-\alpha y^2} \, dy \right] \\ &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\alpha(x^2 + y^2)} \, dx \, dy \end{aligned}$$

$$= \int_0^{2\pi} d\varphi \int_0^\infty r e^{-\alpha r^2} dr$$

Now let $z = \alpha r^2$ so $dz = 2\alpha r dr$.

$$\begin{aligned} &= 2\pi \int_0^\infty \frac{1}{2\alpha} e^{-z} dz \\ &= \frac{\pi}{\alpha} [-e^{-z}]_0^\infty \\ &= \frac{\pi}{\alpha} \end{aligned}$$

So

$$I = \int_{-\infty}^\infty e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}.$$

We can then easily calculate higher moments. If n is odd then

$$\int_{-\infty}^\infty x^n e^{-\alpha x^2} dx = 0$$

as it is the integral of an even function over an even range. If n is even then we use differentiation under the integral sign repeatedly. First

$$\begin{aligned} \int_{-\infty}^\infty x^2 e^{-\alpha x^2} dx &= \int_{-\infty}^\infty -\frac{\partial}{\partial \alpha} e^{-\alpha x^2} dx \\ &= -d\alpha \int_{-\infty}^\infty e^{-\alpha x^2} dx \\ &= -d\alpha \alpha^{-1/2} \sqrt{\pi} \\ &= \frac{1}{2} \alpha^{-3/2} \sqrt{\pi} \\ &= \frac{1}{2} \sqrt{\frac{\pi}{\alpha^3}}. \end{aligned}$$

The fourth moment can then be found in a similar way by differentiating twice.

The most important use of Gaussian integrals is normalising the Gaussian distribution,

$$P(x) = A \exp(-x^2/2\sigma^2).$$

For this to be properly normalised we require

$$A \int_{-\infty}^\infty e^{-x^2/2\sigma^2} dx = 1$$

and so

$$1 = A \sqrt{\frac{\pi}{1/2\sigma^2}} \implies A = \frac{1}{\sqrt{2\pi\sigma^2}}.$$

The most general form of the Gaussian distribution,

$$P(x) = \int_{-\infty}^\infty \exp\left[-\frac{1}{2} \frac{(x-\mu)^2}{\sigma^2}\right] dx,$$

is simply a horizontally shifted version and therefore the normalisation factor is the same.

D Geometric Series

An infinite geometric series is a series of the form

$$S = \sum_{n=0}^{\infty} a^n = 1 + a + a^2 + \dots$$

To evaluate this is fairly simple:

$$\begin{aligned} S &= 1 + a + a^2 + a^3 + \cdots \\ &= 1 + a(1 + a + a^2 + \cdots) \\ &= 1 + aS \end{aligned}$$

which, when rearranged, gives

$$S = \frac{1}{1-a}.$$

E Integral of $x^{(p-1)}/(e^x - 1)$

We wish to calculate the integral

$$\int_0^\infty \frac{x^3}{e^x - 1} dx.$$

We will actually do this for the more general

$$\int_0^\infty \frac{x^{p-1}}{e^x - 1} dx$$

where $p > 1$. Then we have

$$\int_0^\infty \frac{x^{p-1}}{e^x - 1} dx = \int_0^\infty \frac{1}{1 - e^{-x}} e^{-x} x^{p-1} dx$$

recognising this first term as the limit of a geometric series and since $e^{-x} < 1$ for all positive x this becomes

$$\begin{aligned} &= \int_0^\infty e^{-x} \left[\sum_{m=0}^\infty (e^{-x})^m \right] x^{p-1} dx \\ &= \int_0^\infty \sum_{m=0}^\infty e^{-(m+1)x} x^{p-1} dx \end{aligned}$$

since the geometric series is uniformly convergent (where it converges) we can safely swap the sum and the integral:

$$= \sum_{m=0}^\infty \int_0^\infty e^{-(m+1)x} x^{p-1} dx$$

let $n = m + 1$ then

$$= \sum_{n=1}^\infty \int_0^\infty e^{-nx} x^{p-1} dx$$

now making the substitution $y = nx$ so $dy = n dx$ we have

$$\begin{aligned} &= \sum_{n=1}^\infty \int_0^\infty e^{-y} \frac{y^{p-1}}{n^{p-1}} \frac{dy}{n} \\ &= \sum_{n=1}^\infty \frac{1}{n^p} \int_0^\infty e^{-y} y^{p-1} dy \\ &= \zeta(p) \Gamma(p) \end{aligned}$$

where ζ is the Riemann zeta function and Γ is the gamma function. It is not possible to evaluate both of these functions exactly at all values of p , fortunately for the value $p = 4$ that we care about we know that $\zeta(4) = \pi^4/90$ and $\Gamma(4) = 6$ and so

$$\int_0^\infty \frac{x^3}{e^x - 1} dx = \zeta(4) \Gamma(4) = \frac{\pi^4}{15}.$$

Similarly we will need later in the text the integral

$$\int_0^\infty \frac{x^2}{e^x - 1} dx$$

which can be evaluated the same way using $p = 3$ however this is one of those cases where an exact value is not known. We have $\zeta(3) \approx 1.20205$ and $\Gamma(3) = 2^{22}$ so

$$\int_0^\infty \frac{x^2}{e^x - 1} dx \approx 2.4041$$

We will also need the integral

$$\int_0^\infty \frac{x^{1/2}}{e^x - 1} dx.$$

This corresponds to $p = 3/2$ and we have $\Gamma(3/2) = \sqrt{\pi}/2$ and $\zeta(3/2) \approx 2.612$ so

$$\int_0^\infty \frac{x^{1/2}}{e^x - 1} dx \approx 1.306\sqrt{\pi}.$$

²²recall that $\Gamma(n) = (n-1)!$ for $n \in \mathbb{Z}$.