

Thermo

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Almost Out

1 Classical Thermodynamics

1.1 State Variables

The first principle of thermodynamics is that a system composed of a large number of particles which can reach a steady state can be characterised by *state variables*. No progress is made by trying to analyse the behaviour of 10^{23} particles, but progress can be made by analysing these macroscopic properties of the system. These include pressure p , volume V , number of moles of gas n , and temperature T , along with many others. State variables are entirely a property of the system “as it is”, they do not depend at all on how the system managed to reach the state they are in. This may seem obvious for something like V (the volume of a gas doesn’t depend on how it was compressed/expanded to reach that volume), but for other state variables it is less obvious. Other variables, like work done W or heat transfer Q , depend on the method used and so are not state variables.

There are two types of state variables: *intensive* and *extensive*. Intensive state variables remain the same if the system is duplicated (including p and T); extensive state variables double (including V and n). An extensive variable divided by another extensive variable gives an intensive variable (for instance, number of moles per unit volume).

1.2 The 0th Law of Thermodynamics

If two systems A and B are brought into contact so that heat *can* flow between them, but no heat actually flows, the systems are said to be in *thermal equilibrium*. The 0th law states that if A and a third system C are in thermal equilibrium, and A and B are also in thermal equilibrium, then B and C are in thermal equilibrium as well. It stands to reason that there must be a state variable of a system which determines whether or not any

heat will flow between them; this state variable is called the temperature, \mathbf{T} ; the 0th law essentially states that such a quantity exists. Note that for systems not in thermal equilibrium, 0LT does *not* state where the heat will flow to or from, merely whether any heat will flow at all.

Boyle found that the quantity \mathbf{pV} of a gas is constant at a given temperature (for low pressures and far from the liquefaction temperature of the gas). One can then arbitrarily define \mathbf{T} by $\mathbf{pV} \propto \mathbf{T}$. The Celsius scale is then defined by:

$$\mathbf{T}_C(\text{state}) = 100 \frac{\mathbf{pV}|_{\text{state}} - \mathbf{pV}|_{\text{mpw}}}{\mathbf{pV}|_{\text{bpw}} - \mathbf{pV}|_{\text{mpw}}}$$

where the states mpw and bpw correspond to the melting point (0°C) and boiling point (100°C) respectively of water.

1.3 Ideal gases

The above defines $\mathbf{T} \propto \mathbf{pV}$. Because \mathbf{V} is an extensive quantity, we have $\mathbf{V} \propto \mathbf{n}$, so we then have $\mathbf{pV} \propto \mathbf{nT}$. It was initially thought that the proportionality constant would depend on the content of the gas in question (whether it was oxygen or nitrogen, for example), but Avogadro showed that equal volumes of gas (of any content) have equal numbers of molecules, so the proportionality constant should be universal, $R \approx 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$. We thus have:

$$\mathbf{pV} = \mathbf{nRT} = \mathbf{N}k_B\mathbf{T}$$

referred to as an “equation of state” for an “ideal gas”; k_B is simply R/N_A .

Some very basic statistical dynamics gives that $\mathbf{pV} = \frac{1}{3}\mathbf{N}m\langle u^2 \rangle$ (assuming that the gas is monoatomic and the particles do not interact) so the *internal energy* \mathbf{U} (the total energy of the system, here purely kinetic) is given by:

$$\mathbf{U} \equiv \frac{1}{2}\mathbf{N}m\langle u^2 \rangle = \frac{3}{2}\mathbf{pV} = \frac{3}{2}\mathbf{N}k_B\mathbf{T} = \frac{3}{2}\mathbf{nRT}$$

So the kinetic energy of the system is satisfyingly proportional to the temperature, when it is defined as above.

1.3.1 The 1st Law of Thermodynamics

The 1st Law of Thermodynamics essentially states that energy is conserved. There are two different ways in which energy can be transferred to a system

(thus increasing its \mathbf{U}): transferring heat to it, and doing work on it. We therefore have 1LT:

$$d\mathbf{U} = \delta\mathbf{Q} + \delta\mathbf{W}$$

Note that “ $d\mathbf{Q}$ ” is meaningless, as whereas \mathbf{U} takes a specific value that may change, \mathbf{Q} is simply something that can be transferred to a system, so it makes no sense to talk of the “change in heat”. 1LT states that although $\delta\mathbf{Q}$ and $\delta\mathbf{W}$ can take any value at all (including negative values, corresponding to heat transfer *from* the system and work done *by* the system), their sum corresponds to the change in \mathbf{U} of the system.

There are many different types of work that can be done, whenever the system moves in response to an external force. If a gas undergoes compression or expansion, the work done is $\delta\mathbf{W} = -\mathbf{p} d\mathbf{V}$. This is often taken as the archetype of a way of doing work; if other ways of doing work are possible (such as electrochemical work, $\delta\mathbf{W} = v dq$), then simply replace/supplement the $-\mathbf{p} d\mathbf{V}$ term with the extra work term(s).

1.3.2 Heat Capacities

The specific heat capacity is a quantity that satisfies $\delta\mathbf{Q} = C d\mathbf{T}$, and takes different values (C_p and C_V) depending on whether the gas is held at constant \mathbf{p} or constant \mathbf{V} during the heat transfer. Rearranging 1LT and substituting for $\delta\mathbf{Q}$ and $\delta\mathbf{W}$ assuming that the only work possible is gas expansion, we obtain:

$$\begin{aligned} C d\mathbf{T} &= d\mathbf{U} + \mathbf{p} d\mathbf{V} \\ &= \left(\frac{\partial\mathbf{U}}{\partial\mathbf{T}}\right)_{\mathbf{V}} d\mathbf{T} + \left[\left(\frac{\partial\mathbf{U}}{\partial\mathbf{V}}\right)_{\mathbf{T}} + \mathbf{p}\right] d\mathbf{V} \\ &= \frac{3}{2}\mathbf{n}R d\mathbf{T} + \mathbf{p} d\mathbf{V} \end{aligned}$$

where the partial derivatives of \mathbf{U} are deduced from $\mathbf{U} = \frac{3}{2}\mathbf{n}R\mathbf{T}$. This makes it clear that $C_p > C_V$, as in the latter case heat is only used to increase \mathbf{U} and thus \mathbf{T} , whereas at constant pressure the heat may also be converted into work – so more heat is required to cause a given change in \mathbf{T} . At constant volume, we have $d\mathbf{V} = 0$ and so:

$$C_V = \frac{3}{2}\mathbf{n}R$$

Whereas at constant pressure, we have:

$$C_p = \frac{3}{2}\mathbf{n}R + \mathbf{p} \left(\frac{\partial\mathbf{V}}{\partial\mathbf{T}}\right)_{\mathbf{p}} = C_V + \mathbf{p} \frac{\mathbf{n}R}{\mathbf{p}}$$

$$= C_V + nR = \frac{5}{2}nR$$

We recall that both of these expressions apply only for an ideal monatomic gas.

1.3.3 Expansions

The changes in state functions during expansions can also be derived. For an *isothermal* expansion, the temperature is constant (the gas may be connected to a reservoir), and so $dU = 0$ and $\delta Q = p dV$. The heat transferred to bring about this expansion is then:

$$Q = \int \delta Q = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \left(\frac{V_2}{V_1} \right)$$

where T can be brought outside the integral because it is constant in this process. The work done in this expansion is the negative of the above quantity, so that $\Delta U = 0$. On a p - V diagram, the previous calculation corresponds to the area under an isotherm at temperature T .

Adiabatic expansions have no transfer of heat, and so all the energy needed to do expansion work is drained from the internal energy U . We have:

$$\begin{aligned} \delta W &= dU = C_V dT = -p dV \\ \frac{C_V}{nR} (p dV + V dp) &= -p dV \\ \underbrace{(C_V + nR)}_{C_p} p dV + C_V V dp &= 0 \\ \gamma \frac{dV}{V} + \frac{dp}{p} &= 0 \quad \text{where } \gamma \equiv \frac{C_p}{C_V} > 1 \\ pV^\gamma &= \text{const.} \end{aligned}$$

Using the ideal gas law we also see that $V^{\gamma-1}T$ and $p^{1-\gamma}T^\gamma$ are also constant in adiabatic expansions. The quantity γ is called the *specific heat ratio*, and for a monoatomic gas is equal to $5/3$. The amount of work done in an adiabatic expansion is simply equal to $\Delta U = \frac{3}{2}nR\Delta T$.

1.4 2nd Law of Thermodynamics

The two expansion processes in the previous section were *reversible* processes, meaning that the process could be “nudged” along in infinitesimal steps which could easily be reversed. There are however many processes which are

empirically known to be *irreversible*, even though 1LT does not forbid them. If a partition, between a volume full of gas and an empty space, is removed, then the gas irreversibly moves to fill the space (this process is called *Joule expansion*); it never retreats back.

Irreversible processes are fundamentally driven by probability: the probability that each molecule is on one half of the box is 2^{-N} , whereas the probability that there are $N/2$ on each side is astronomically more probable (by a factor $N!/(N/2)!$). However, before this was known, thermodynamics was all about heat engines, and Clausius and Kelvin both came up with (equivalent) empirical observations of 2LT:

No process whose only effect is heat transfer from cold to hot is possible

No process whose only effect is complete conversion of heat to work is possible

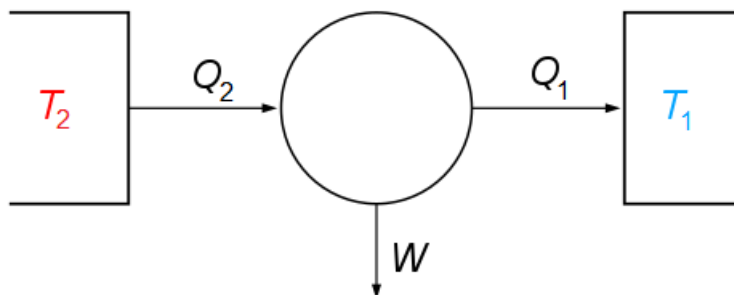
Another, less formal expression of 2LT is that if no extra work is being done, heat flows from hot to cold. In the same way as N1L is a special case of N2L, 0LT (no spontaneous heat transfer between bodies at same temperature) is thus a special case of 2LT.

1.4.1 Carnot Cycle

Carnot demonstrated that:

- a reversible heat engine (a machine that converts heat transferred from a reservoir and converts it into work and wasted heat) is theoretically possible
- all reversible heat engines are equally *efficient* (defined shortly)
- irreversible heat engines are less efficient.

The general diagram for a heat engine is:



We thus see that that Kelvin's version of 2LT is saying that $Q_1 \neq 0$. The *efficiency* of a heat engine is defined by $\eta \equiv W/Q_2 = 1 - Q_1/Q_2$. The Carnot cycle has 4 stages:

1. **Isothermal expansion** from V_A to V_B , at T_2 . In this stage, the work done on the gas is $nRT_2 \ln(V_A/V_B) < 0$ (work is actually being done *by* the gas to cause expansion); the heat $Q_2 = nRT_2 \ln(V_B/V_A)$, keeping U constant.
2. **Adiabatic expansion** from V_B to V_C , between T_2 and T_1 . The work done by the gas simply $\frac{3}{2}nR(T_2 - T_1)$; $Q = 0$ by definition of an adiabatic expansion
3. **Isothermal contraction** from V_C to V_D , at T_1 . Here work is done on the gas $nRT_1 \ln(V_C/V_D)$. Now the actual heat transferred *to* the engine is $nRT_1 \ln(V_D/V_C)$, which is negative, but in the diagram Q_1 is actually defined as the amount of heat which flows *out* of the system, so $Q_1 = nRT_1 \ln(V_C/V_D)$. If you prefer, Q_1 is the *magnitude* of the heat transfer.
4. **Adiabatic contraction** from V_D to V_A between T_1 and T_2 . The work done is $\frac{3}{2}nR(T_1 - T_2)$, which again is negative; $Q = 0$.

The signs are often difficult to keep track of, so try to understand which direction heat is flowing and work is being done; note that $V_C > (V_B, V_D) > V_A$. Adding up all the stages, we obtain that the *total* work done *by* the heat engine (the *negative* of the total work done on the system W_{tot}) is:

$$\begin{aligned} W &= nRT_2 \ln\left(\frac{V_B}{V_A}\right) - \frac{3}{2}nR(T_2 - T_1) + nRT_1 \ln\left(\frac{V_D}{V_C}\right) + \frac{3}{2}nR(T_2 - T_1) \\ &= nRT_2 \ln\left(\frac{V_B}{V_A}\right) + nRT_1 \ln\left(\frac{V_D}{V_C}\right) = Q_2 - Q_1 \end{aligned}$$

Now from the formulae for adiabatic expansions, pV^γ and so $\Rightarrow V^{\gamma-1}T$ are constant, for steps 2 and 4. Thus:

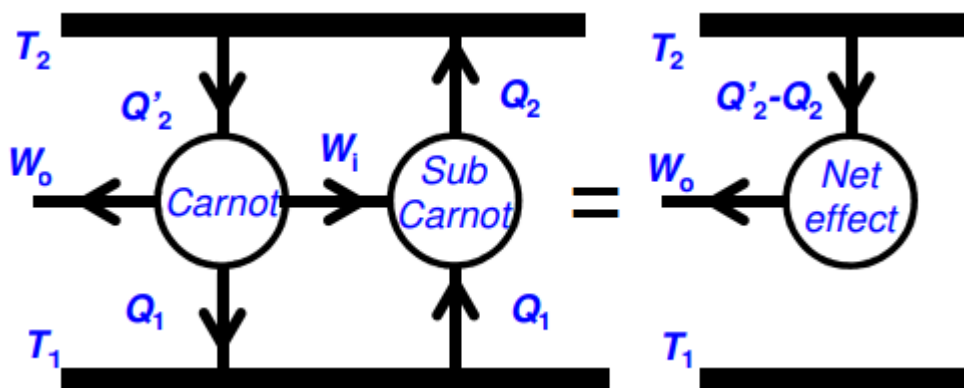
$$\begin{aligned} T_2 V_B^{\gamma-1} &= T_1 V_C^{\gamma-1} & T_1 V_D^{\gamma-1} &= T_2 V_A^{\gamma-1} \\ \Rightarrow \frac{V_B}{V_C} &= \left(\frac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}} & \frac{V_D}{V_A} &= \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} \\ \Rightarrow \frac{V_B}{V_C} &= \frac{V_A}{V_D} \Rightarrow \frac{V_B}{V_A} &= \frac{V_C}{V_D} \end{aligned}$$

$$\Rightarrow \frac{Q_2}{T_2} = nR \ln \left(\frac{V_B}{V_A} \right) = nR \ln \left(\frac{V_C}{V_D} \right) = \frac{Q_1}{T_1}$$

$$\Rightarrow \eta = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

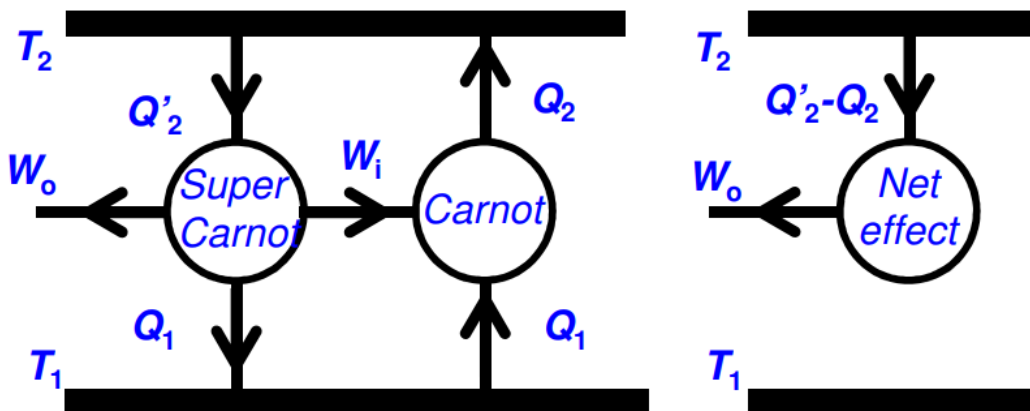
giving an important formula for the efficiency of a heat engine.

The proof that all reversible heat engines are equally efficient is as follows:



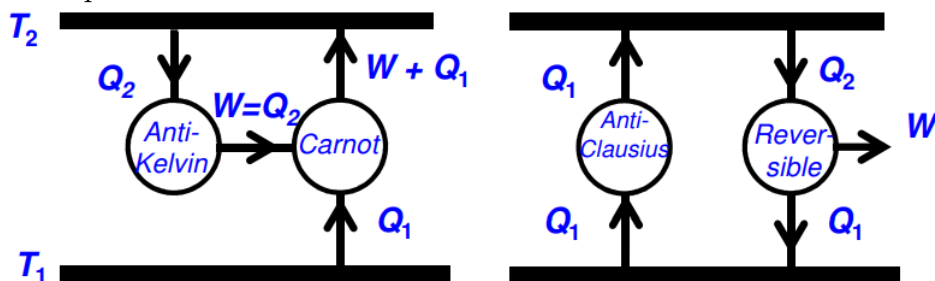
Suppose there exists a “sub-Carnot” engine, which is reversible but less efficient than a regular Carnot engine. If we were to use a Carnot engine to run another Carnot engine backwards, then we would have $Q'_2 = Q_2$ and $W_o = 0$. But if we use a Carnot engine to run a *sub-Carnot* engine backwards with equal Q_1 s, then $Q'_2 > Q_2$ and there will be some positive W_o left over. The net effect of this setup is that heat is being completely converted into work, which violates Kelvin’s 2LT. All that has been proven at this stage is that reversible heat engines cannot be *less* efficient than Carnot’s.

It is now shown that no engine, reversible or not, can be *more* efficient than Carnot’s. Suppose there exists a “super-Carnot” engine (of any reversibility), and we use that to run a Carnot engine backwards:



As before, the higher efficiency of the super-Carnot engine means that more heat is drawn from the T_2 reservoir and more work is obtained for the same wasted heat Q_1 as a regular Carnot engine. As such, the net effect of using a super-Carnot engine to run a regular Carnot engine is again that heat from T_2 is completely converted into work, violating Kelvin's 2LT. The overall result is that all *reversible* heat engines have the *same* efficiency as Carnot's, and all *irreversible* heat engines have *at most* the same efficiency as Carnot's.

It is now shown that Kelvin's 2LT (\mathfrak{K}) is equivalent to Clausius' (\mathfrak{C}) (that heat cannot be transferred from cold to hot alone), by showing that violation of one implies violation of the other.



In the first diagram, we see that a device which violates Kelvin's 2LT can be coupled to a Carnot engine and cause a net heat transfer of Q_1 from T_1 to T_2 , violating Clausius' 2LT. Logically this shows that $\neg\mathfrak{K} \Rightarrow \neg\mathfrak{C}$. The second diagram shows a Clausius-violating engine in tandem with a Carnot engine, with the net effect being the conversion of heat $Q_2 - Q_1$ purely into work, in violation of Kelvin, thus $\neg\mathfrak{C} \Rightarrow \neg\mathfrak{K}$. Combining the results we have:

$$\neg\mathfrak{C} \iff \neg\mathfrak{K} \quad \mathfrak{C} \iff \mathfrak{K}$$

that is, the two are equivalent (note that both ways around are needed to show this).

There are other things one can do with a Carnot cycle by running it backwards, leading to different definitions of the efficiency. One can use it as a *heat pump*, in which case the efficiency is the heat moved into the hot reservoir (like a house) divided by the work done: $\eta \equiv Q_2/W = Q_2/(Q_2 - Q_1) = T_2/(T_2 - T_1)$. As before, this is the maximum efficiency of a heat pump, and it is clearly greater than 1. Alternatively, one can use it as a refrigerator, in which case $\eta \equiv Q_1/W = Q_1/(Q_2 - Q_1) = T_1/(T_2 - T_1)$.

Real heat engines are irreversible, due to heat leaking, friction, and turbulence, and so they have an efficiency less than the theoretical maximum. Further, their composition often changes throughout the cycle, and the temperatures of the reservoirs may not be fixed. These engines are often approx-

imated using “Air Standard” cycles (e.g. Otto and Stirling), which do not run in the same way as Carnot’s.

1.4.2 Classical Entropy

At this point we return to the original sign convention for the heat, whereby heat is transferred *into* the system counts as positive. As such Q_2 represents positive heat and Q_1 represents negative heat; in other words $Q_{\text{tot}} = Q_2 - Q_1$. As $Q_2/T_2 = Q_1/T_1$, we can also write:

$$\oint_{\text{Carnot}} \frac{\delta Q}{T} = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0$$

As Q_2 and Q_1 have the same relationship for all reversible heat engines, we can write that:

$$\oint \frac{\delta Q_{\text{rev}}}{T} \equiv 0$$

By contrast, *irreversible* heat engines are *at most* as efficient than reversible ones, and so have a larger Q_1 for the same Q_2 (and a smaller amount of work done). Remembering that Q_1 corresponds to *negative* heat into the system, we therefore have:

$$\oint \frac{\delta Q}{T} \leq 0$$

which is *Clausius’ Theorem* for any cycle; the equality applies if the cycle is reversible. Breaking the penultimate integral up into two stages (where the break comes at an arbitrary point), we then have:

$$\oint \frac{\delta Q_{\text{rev}}}{T} = \int_{A; 1}^B \frac{\delta Q_{\text{rev}}}{T} + \int_{B; 2}^A \frac{\delta Q_{\text{rev}}}{T} = 0 \Rightarrow \int_{A; 1}^B \frac{\delta Q_{\text{rev}}}{T} = \int_{A; 2}^B \frac{\delta Q_{\text{rev}}}{T}$$

where the 1 and 2 next to the lower bound of the integrals refers to two different (though both reversible) integration paths. We see that the integral of $\delta Q_{\text{rev}}/T$ is independent of the path. This means that the integrand must correspond to the differential of some (extensive) state variable, call it, oh I don’t know, dS . So $\int_A^B \delta Q_{\text{rev}}/T = \int_A^B dS = S(B) - S(A)$, regardless of the (reversible) path taken. We note that adiabatic processes, which have $\delta Q_{\text{rev}} = 0$, are also *isoentropic*, having $dS = 0$. Also, if we back off from the limit to $\Delta S = \Delta Q_{\text{rev}}/T \Rightarrow 1/T = \Delta S/\Delta Q_{\text{rev}}$ we obtain (abusing notation somewhat):

$$\frac{1}{T} = \left(\frac{\partial S}{\partial Q} \right)_{\text{rev}}$$

What is the entropy change if an *irreversible* path is taken? Consider going from A to B irreversibly, but back from B to A reversibly. According to Clausius' theorem:

$$\int_A^B \frac{\delta Q_{\text{irrev}}}{\mathbf{T}} + \int_B^A \frac{\delta Q_{\text{rev}}}{\mathbf{T}} \leq 0 \Rightarrow \int_A^B \frac{\delta Q_{\text{irrev}}}{\mathbf{T}} \leq \int_A^B d\mathbf{S} \Rightarrow \frac{\delta Q_{\text{irrev}}}{\mathbf{T}} \leq d\mathbf{S}$$

with equality in the limit of reversibility. To find the entropy change before and after an *irreversible* process, we **cannot** simply take $\int \delta Q_{\text{irrev}}/\mathbf{T}$, as this is not an entropy change; instead we must find a *reversible* process which links the same before-and-after states, and calculate $\int \delta Q_{\text{rev}}/\mathbf{T}$ for *that* process. However, thermodynamics does not tell you how to do this, one relies on experience.

For a thermally isolated system, $\delta Q_{\text{irrev}} = 0$, and so using the above equation we have another phrasing of 2LT:

$$d\mathbf{S} \geq 0 \text{ for isolated systems}$$

It is interesting to note that the entire Universe is a thermally isolated system, and so *the entropy of the Universe can never decrease*.

2 Analytical Thermodynamics

2.1 The Master Equation

Using 1LT and 2LT, we may then write the *master equation*:

$$d\mathbf{U} = \mathbf{T} d\mathbf{S} - \mathbf{p} d\mathbf{V}$$

where $-\mathbf{p}d\mathbf{V}$ may be replaced/supplemented by other forms of work. Note that this equation contains only state variables, and so it must be true for all processes, reversible or ir-, even though it was constructed for reversible processes. Rearranging the master equation, we have for an ideal gas:

$$d\mathbf{S} = \frac{1}{\mathbf{T}} d\mathbf{U} + \frac{\mathbf{p}}{\mathbf{T}} d\mathbf{V} = C_V \frac{d\mathbf{T}}{\mathbf{T}} + nR \frac{d\mathbf{V}}{\mathbf{V}} \Rightarrow \Delta\mathbf{S}(\mathbf{T}, \mathbf{V}) = C_V \ln\left(\frac{\mathbf{T}}{\mathbf{T}_0}\right) + nR \ln\left(\frac{\mathbf{V}}{\mathbf{V}_0}\right)$$

which is the change in entropy for an ideal gas expanding or being heated.

From the Master Equation we can identify:

$$\left(\frac{\partial \mathbf{U}}{\partial \mathbf{S}}\right)_{\mathbf{V}} = \mathbf{T} \qquad \left(\frac{\partial \mathbf{U}}{\partial \mathbf{V}}\right)_{\mathbf{S}} = -\mathbf{p}$$

from which we can obtain:

$$\left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}}\right)_{\mathbf{U}} \equiv -\left(\frac{\partial \mathbf{S}}{\partial \mathbf{U}}\right)_{\mathbf{V}} \left(\frac{\partial \mathbf{U}}{\partial \mathbf{V}}\right)_{\mathbf{S}} = \frac{\mathbf{p}}{\mathbf{T}}$$

in which the first equivalence comes from the reciprocity and reciprocal theorems from partial differential calculus. Furthermore, using the equality of mixed partial derivatives, we can write:

$$\left(\frac{\partial \mathbf{T}}{\partial \mathbf{V}}\right)_{\mathbf{S}} \equiv -\left(\frac{\partial \mathbf{p}}{\partial \mathbf{S}}\right)_{\mathbf{V}}$$

an example of a *Maxwell Relation*.

2.2 Thermodynamic Potentials

It is easiest to use $\mathbf{U}(\mathbf{S}, \mathbf{V})$ when the independent variables of interest are \mathbf{S} and \mathbf{V} . Practically, however, it is often easier to control other variables, such as \mathbf{p} or \mathbf{T} , in which case there are certain other state variables which are more useful to consider. Each of these also comes with its own Maxwell Relation as a bonus.

2.2.1 Enthalpy $\mathbf{H}(\mathbf{S}, \mathbf{p}) \equiv \mathbf{U} + \mathbf{pV}$

In chemical reactions, the pressure is usually constant, and it is easier if we use a state variable whose differential depends on $d\mathbf{p}$. Defining $\mathbf{H} \equiv \mathbf{U} + \mathbf{pV}$, we have:

$$d\mathbf{H} = \mathbf{T}d\mathbf{S} + \mathbf{V}d\mathbf{p}$$

Giving the relations:

$$\left(\frac{\partial \mathbf{H}}{\partial \mathbf{S}}\right)_{\mathbf{p}} = \mathbf{T} \quad \left(\frac{\partial \mathbf{H}}{\partial \mathbf{p}}\right)_{\mathbf{S}} = \mathbf{V} \quad \Rightarrow \quad \left(\frac{\partial \mathbf{T}}{\partial \mathbf{p}}\right)_{\mathbf{S}} \equiv \left(\frac{\partial \mathbf{V}}{\partial \mathbf{S}}\right)_{\mathbf{p}}$$

For changes at constant pressure, we have $d\mathbf{H} = \mathbf{T}d\mathbf{S} = \delta\mathbf{Q}$, and so:

$$C_p = \left(\frac{\partial \mathbf{H}}{\partial \mathbf{T}}\right)_{\mathbf{p}}$$

It can also be shown that, for continuous flow processes, the difference between the enthalpies of a quantity of outgoing and ingoing fluid is simply equal to the heat and work done on it: $\Delta\mathbf{H} = \mathbf{Q} + \mathbf{W}$.

2.2.2 Helmholtz Free Energy $\mathbf{F}(\mathbf{T}, \mathbf{V}) \equiv \mathbf{U} - \mathbf{T}\mathbf{S}$

It is often not easy to use \mathbf{S} as a variable, as it is difficult to “control”. One state variable which achieves this is \mathbf{F} ; from its definition we have:

$$d\mathbf{F} = -\mathbf{S}d\mathbf{T} - \mathbf{p}d\mathbf{V}$$

from which we obtain:

$$\left(\frac{\partial \mathbf{F}}{\partial \mathbf{T}}\right)_{\mathbf{V}} = -\mathbf{S} \quad \left(\frac{\partial \mathbf{F}}{\partial \mathbf{V}}\right)_{\mathbf{T}} = -\mathbf{p} \quad \left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}}\right)_{\mathbf{T}} \equiv \left(\frac{\partial \mathbf{p}}{\partial \mathbf{T}}\right)_{\mathbf{V}}$$

Alternatively, at constant temperature and volume, and under reversible conditions, we can use the original definition to give:

$$\begin{aligned} d\mathbf{F} &= d\mathbf{U} - \mathbf{T}d\mathbf{S} = \delta\mathbf{Q} + \delta\mathbf{W} - \mathbf{T}d\mathbf{S} \\ &= -\delta\mathbf{Q}_{\text{surr}} + \delta\mathbf{W} - \mathbf{T}d\mathbf{S}_{\text{sys}} = -\mathbf{T}d\mathbf{S}_{\text{univ}} + \delta\mathbf{W} \\ &\leq \delta\mathbf{W} \\ \Rightarrow -\delta\mathbf{W} &\leq -d\mathbf{F} \end{aligned}$$

This result is significant because $-\delta\mathbf{W}$ is the work done by the system. We see therefore that $-d\mathbf{F}$ represents the maximum amount of energy that can be converted into work. That this is not equal to $-d\mathbf{U}$ is a statement of 2LT: some of the energy must be converted to heat.

It can be shown that, under conditions of constant \mathbf{T} and \mathbf{V} , the entropy change of the universe $d\mathbf{S}_{\text{univ}} = -d\mathbf{F}/\mathbf{T}$, and so under these conditions \mathbf{F} may only decrease.

2.2.3 Gibbs Free Energy $\mathbf{G}(\mathbf{p}, \mathbf{T}) = \mathbf{U} - \mathbf{T}\mathbf{S} + \mathbf{p}\mathbf{V} = \mathbf{H} + \mathbf{p}\mathbf{V}$

The easiest quantities to manipulate are usually \mathbf{p} and \mathbf{T} , so it is often useful to use \mathbf{G} , which has:

$$d\mathbf{G} = \mathbf{V}d\mathbf{p} - \mathbf{S}d\mathbf{T}$$

Thus \mathbf{G} is conserved in all processes which are both isobaric and isothermal, which usefully includes phase transitions. We obtain:

$$\left(\frac{\partial \mathbf{G}}{\partial \mathbf{p}}\right)_{\mathbf{T}} = \mathbf{V} \quad \left(\frac{\partial \mathbf{G}}{\partial \mathbf{T}}\right)_{\mathbf{p}} = -\mathbf{S} \quad \Rightarrow \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}}\right)_{\mathbf{p}} \equiv -\left(\frac{\partial \mathbf{S}}{\partial \mathbf{p}}\right)_{\mathbf{T}}$$

The final Maxwell relations. For convenience these are listed again here:

$$\left(\frac{\partial \mathbf{T}}{\partial \mathbf{V}}\right)_{\mathbf{S}} \equiv -\left(\frac{\partial \mathbf{p}}{\partial \mathbf{S}}\right)_{\mathbf{V}} \quad \left(\frac{\partial \mathbf{T}}{\partial \mathbf{p}}\right)_{\mathbf{S}} \equiv \left(\frac{\partial \mathbf{V}}{\partial \mathbf{S}}\right)_{\mathbf{p}}$$

$$\left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}}\right)_{\mathbf{T}} \equiv \left(\frac{\partial \mathbf{p}}{\partial \mathbf{T}}\right)_{\mathbf{V}} \qquad \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}}\right)_{\mathbf{p}} \equiv -\left(\frac{\partial \mathbf{S}}{\partial \mathbf{p}}\right)_{\mathbf{T}}$$

Note that these all involve all 4 of the original natural variables ($\mathbf{T}, \mathbf{S}, \mathbf{p}, \mathbf{V}$), and that (\mathbf{p}, \mathbf{V}) and (\mathbf{T}, \mathbf{S}) are never the pairs involved in the derivative. In each case, the “lower” two variables are the natural variables of the thermodynamic potential from which the relation is derived; for example the first term has \mathbf{V} and \mathbf{S} as the “lower” two variables, and so must be derived from \mathbf{U} , which has \mathbf{V} and \mathbf{S} as its natural variables. Also, it is important to note that nowhere in the derivation of these relations was the ideal gas law used – they are true regardless of the equation of state of the material in question.

One can easily show that extra forms of work ($\delta \mathbf{W}_+ \not\equiv -\mathbf{p}d\mathbf{V}$) would remain tagged on the end of the $d\mathbf{G}$ equation above. Thus at constant pressure and temperature (not exactly rare conditions), $d\mathbf{G} = \delta \mathbf{W}_+$. Note that these extra forms of work are done *on* the system, and so $-d\mathbf{G}$ is the maximum *non- \mathbf{pV}* work that can be done *by* a system.

It can be shown that, under conditions of constant \mathbf{T} and \mathbf{p} , the entropy change of the universe $d\mathbf{S}_{\text{univ}} = -d\mathbf{G}/\mathbf{T}$, and so under these conditions \mathbf{G} may only decrease. Note that the corresponding condition for \mathbf{F} was at constant *volume* rather than constant *pressure*.

2.2.4 Summary of Thermodynamic Potentials

It turns out that in statistical thermodynamics, \mathbf{F} is usually the easiest quantity to work with, along with its natural variables \mathbf{T} and \mathbf{V} . As such, it is useful to derive the other three potentials in terms of \mathbf{F} . This is done below:

$$\begin{aligned} \mathbf{U} &= \mathbf{F} + \mathbf{T}\mathbf{S} = \mathbf{F} - \mathbf{T} \left(\frac{\partial \mathbf{F}}{\partial \mathbf{T}}\right)_{\mathbf{V}} \\ &= -\mathbf{T}^2 \left(\frac{\partial \mathbf{F}/\mathbf{T}}{\partial \mathbf{T}}\right)_{\mathbf{V}} \\ \mathbf{H} &= \mathbf{F} + \mathbf{T}\mathbf{S} + \mathbf{p}\mathbf{V} = \mathbf{F} - \mathbf{T} \left(\frac{\partial \mathbf{F}}{\partial \mathbf{T}}\right)_{\mathbf{V}} - \mathbf{V} \left(\frac{\partial \mathbf{F}}{\partial \mathbf{V}}\right)_{\mathbf{T}} \\ &= \mathbf{F} - \mathbf{T}^2 \left(\frac{\partial \mathbf{F}/\mathbf{T}}{\partial \mathbf{T}}\right)_{\mathbf{V}} - \mathbf{V}^2 \left(\frac{\partial \mathbf{F}/\mathbf{V}}{\partial \mathbf{V}}\right)_{\mathbf{T}} \\ \mathbf{G} &= \mathbf{F} + \mathbf{p}\mathbf{V} = \mathbf{F} - \mathbf{V} \left(\frac{\partial \mathbf{F}}{\partial \mathbf{V}}\right)_{\mathbf{T}} \\ &= \mathbf{F} - \mathbf{V}^2 \left(\frac{\partial \mathbf{F}/\mathbf{V}}{\partial \mathbf{V}}\right)_{\mathbf{T}} \end{aligned}$$

2.3 Applications of Analytical Thermodynamics

2.3.1 Specific Heat Capacities

The difference between the specific heat capacities of an ideal gas was derived earlier, but a more general expression exists, without reference to an equation of state:

$$\begin{aligned} C_p - C_V &= \lim_{\delta \mathbf{T} \rightarrow 0} \left(\left. \frac{\delta \mathbf{Q}}{\delta \mathbf{T}} \right|_{\mathbf{p}} - \left. \frac{\delta \mathbf{Q}}{\delta \mathbf{T}} \right|_{\mathbf{v}} \right) \\ &= T \lim_{\delta \mathbf{T} \rightarrow 0} \left(\left. \frac{\delta \mathbf{S}}{\delta \mathbf{T}} \right|_{\mathbf{p}} - \left. \frac{\delta \mathbf{S}}{\delta \mathbf{T}} \right|_{\mathbf{v}} \right) = T \left[\left(\frac{\partial \mathbf{S}}{\partial \mathbf{T}} \right)_{\mathbf{p}} - \left(\frac{\partial \mathbf{S}}{\partial \mathbf{T}} \right)_{\mathbf{v}} \right] \end{aligned}$$

Now there are no Maxwell relations involving $\partial \mathbf{S} / \partial \mathbf{T}$, so we must take a different approach. Consider taking $\mathbf{S} = \mathbf{S}(\mathbf{T}, \mathbf{V})$, and so:

$$\begin{aligned} d\mathbf{S} &= \left(\frac{\partial \mathbf{S}}{\partial \mathbf{T}} \right)_{\mathbf{v}} d\mathbf{T} + \left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}} \right)_{\mathbf{T}} d\mathbf{V} \\ \Rightarrow \left(\frac{\partial \mathbf{S}}{\partial \mathbf{T}} \right)_{\mathbf{p}} &= \left(\frac{\partial \mathbf{S}}{\partial \mathbf{T}} \right)_{\mathbf{v}} + \left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}} \right)_{\mathbf{T}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}} \right)_{\mathbf{p}} \\ \Rightarrow \left(\frac{\partial \mathbf{S}}{\partial \mathbf{T}} \right)_{\mathbf{p}} - \left(\frac{\partial \mathbf{S}}{\partial \mathbf{T}} \right)_{\mathbf{v}} &= \left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}} \right)_{\mathbf{T}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}} \right)_{\mathbf{p}} \\ \Rightarrow C_p - C_V &= \mathbf{T} \left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}} \right)_{\mathbf{T}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}} \right)_{\mathbf{p}} \\ &= \mathbf{T} \left(\frac{\partial \mathbf{p}}{\partial \mathbf{T}} \right)_{\mathbf{v}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}} \right)_{\mathbf{p}} \end{aligned}$$

where a Maxwell relation has been used in the final step. For an ideal gas, the first derivative gives $\mathbf{n}R/\mathbf{V}$, and the second gives $\mathbf{n}R/\mathbf{p}$, giving $C_p - C_V = \mathbf{T} \mathbf{n}^2 R^2 / \mathbf{p} \mathbf{V} = \mathbf{n}R$, as before.

2.3.2 Expansivities and Compressibilities

Expansivities (β) measure fractional change in volume per change in temperature. Depending on external conditions, we have the *isobaric* and *adiabatic* expansivities as:

$$\beta_p \equiv \frac{1}{\mathbf{V}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}} \right)_{\mathbf{p}} \qquad \beta_s \equiv \frac{1}{\mathbf{V}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}} \right)_{\mathbf{s}}$$

respectively. Compressibilities (κ) measure fractional change in volume per change in *pressure*. The *isothermal* and *adiabatic* compressibilities are given by:

$$\kappa_T \equiv -\frac{1}{\mathbf{V}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{p}} \right)_{\mathbf{T}} \quad \kappa_S \equiv -\frac{1}{\mathbf{V}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{p}} \right)_{\mathbf{S}}$$

These quantities enable another expression for the difference between heat capacities:

$$\begin{aligned} C_p - C_V &= \mathbf{T} \left(\frac{\partial \mathbf{p}}{\partial \mathbf{T}} \right)_{\mathbf{V}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}} \right)_{\mathbf{p}} \\ &= \mathbf{T} \left[- \left(\frac{\partial \mathbf{p}}{\partial \mathbf{V}} \right)_{\mathbf{T}} \left(\frac{\partial \mathbf{V}}{\partial \mathbf{T}} \right)_{\mathbf{p}} \right] [\mathbf{V} \beta_p] \\ &= \mathbf{T} \left[\frac{1}{\mathbf{V} \kappa_T} \mathbf{V} \beta_p \right] \mathbf{V} \beta_p \\ &= \frac{\mathbf{T} \mathbf{V} \beta_p^2}{\kappa_T} \end{aligned}$$

which may be more useful if these quantities are easier (or most accurate) to measure.

2.3.3 Elastic Wires and Surfaces

An elastic wire has the master equation $d\mathbf{U} = \mathbf{T}d\mathbf{S} + \mathcal{F}dx$, where \mathcal{F} is the tension and x is the extension. Incidentally, this gives the relations:

$$\left(\frac{\partial \mathbf{U}}{\partial \mathbf{S}} \right)_x = \mathbf{T} \quad \left(\frac{\partial \mathbf{U}}{\partial x} \right)_{\mathbf{S}} = \mathcal{F} \quad \left(\frac{\partial \mathbf{T}}{\partial x} \right)_{\mathbf{S}} = \left(\frac{\partial \mathcal{F}}{\partial \mathbf{S}} \right)_x$$

Wires have the further variables A the cross-sectional area; L the unstretched length;

$$Y \equiv \frac{L}{A} \left(\frac{\partial \mathcal{F}}{\partial x} \right)_{\mathbf{T}} \quad \alpha \equiv \frac{1}{L} \left(\frac{\partial x}{\partial \mathbf{T}} \right)_{\mathcal{F}}$$

the Young's modulus and the coefficient of thermal expansion.

Similarly, elastic surfaces have $d\mathbf{U} = \mathbf{T}d\mathbf{S} + \gamma dA$, where γ is the surface tension.

3 Phase Transitions

3.1 Van der Waals Equation

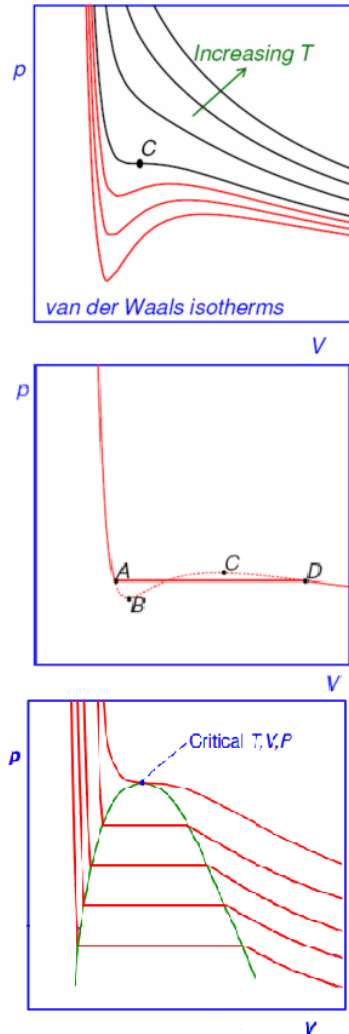
There are two factors that the derivation of the ideal gas law does not take into account: finite molecular volume, and intermolecular forces. Van der Waals took account of the former by replacing \mathbf{V} with $\mathbf{V} - \mathbf{n}b$, where in practice b is a material-dependent experimentally-derived value. The net effect of the intermolecular forces is that they reduce the frequency with which molecules collide with the wall, in a manner proportional to $\rho^2 \propto (\mathbf{n}/\mathbf{V})^2$. As such, we have the modified equation of state:

$$\left(\mathbf{p} + \frac{a\mathbf{n}^2}{\mathbf{V}^2} \right) (\mathbf{V} - \mathbf{n}b) = \mathbf{n}R\mathbf{T}$$

Whereas the ideal gas isotherms were simply hyperbolae on a $\mathbf{p} - \mathbf{V}$ diagram, vdW isotherms are sort of cubic, and look like the figure on the left. We see that at high \mathbf{T} , the isotherms do indeed look roughly hyperbolic. At a certain intermediate *critical temperature* \mathbf{T}_c , there is a point of inflection in the isotherm, described as the *critical point* $(\mathbf{p}_c, \mathbf{V}_c)$. By calculating $(\frac{\partial \mathbf{p}}{\partial \mathbf{V}})_{\mathbf{T}} = 0$ and $(\frac{\partial^2 \mathbf{p}}{\partial \mathbf{V}^2})_{\mathbf{T}} = 0$ from the VdW equation, it can be shown that:

$$\mathbf{V}_c = 3\mathbf{n}b \quad \mathbf{T}_c = \frac{8a}{27b^2} \quad \mathbf{p}_c = \frac{a}{27b^2}$$

At low $\mathbf{T} < \mathbf{T}_c$, however, there is a significant “dipping” observed. To the left of the dip, there is little volume change in response to continually increasing pressure – this corresponds to a *liquid*. To the right of the dip, the graph begins to look hyperbolic again – a gas. In between, though, we encounter a region where if the pressure is increased, the volume *also increases*; in other words $\kappa_T < 0$. This is not actually what happens – this prediction is a shortcoming of the vdW equation. It is corrected by drawing a horizontal line to replace the dip, for which there is an equilibrium between the liquid



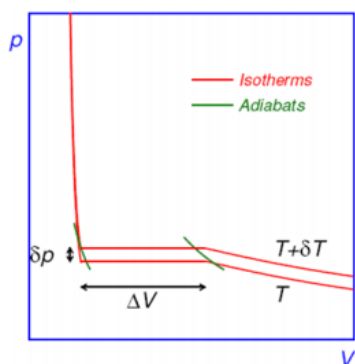
and gaseous phases.

If one were to hypothetically travel along the closed path ABCDA (at constant temperature), there must be no overall change in \mathbf{F} or \mathbf{G} , as these are state variables. $d\mathbf{F} = -p d\mathbf{V}$ and $d\mathbf{G} = \mathbf{V} dp$, so if $\Delta\mathbf{F}$ and $\Delta\mathbf{G}$ are to be 0, we require $\oint p d\mathbf{V} = 0$. As such, the Maxwell construction is drawn so that the area under the vdW curve is 0, as shown; the pressure at which this line is drawn is the *vapour pressure* of the substance at that temperature. By taking the envelope of the Maxwell constructions at different temperatures, we find a sort of hill, whose peak is at the critical point, below which the substance is in equilibrium between gas and liquid. Above T_c , the substance cannot form a liquid. Below T_c , the substance is either liquid (left of the hill), gas (right of the hill) (also known as a *vapour* when below T_c), or in equilibrium therebetwixt (under the hill).

Generally phase changes require nucleation sites, but if very pure, a liquid can be superheated (AB) and a gas can be supercooled (DC). T_c is the highest temperature at which liquid and gas can coexist.

3.2 Phase Diagrams

Phase diagrams are usually p - T diagrams. Lines represent sets of (p, T) points at which two different phases coexist. The liquid-gas line terminates at the critical point, and begins at the end of the solid-liquid line at the *triple point* of the substance, where all three phases coexist. Usually, the phase transition lines have a positive slope. As such, at higher pressure, a greater temperature is generally required to bring about a phase transition. [Water is unusual in that the solid-liquid line has a *negative* slope, which is a consequence of the unusual property that ice has a lower density than liquid water.] The gradient of this line is given by the *Clausius-Clapeyron Equation*, derived below.



When a substance reversibly goes from gas to liquid (say), its entropy decreases, so in order for the total entropy of the Universe to remain constant, *latent heat* $L \equiv T_{pt} \Delta S_{pt}$ must be given out to the surroundings. Consider connecting two Maxwell constructions with adiabats, as shown. This forms a Carnot cycle, whose efficiency is given by $\delta W / \delta Q$. Now δW is equal to $\delta p \Delta V$, where ΔV is the change in volume over the phase change (note that it is temperature dependent), and δQ is simply given by L , so $\eta = \delta p \Delta V / L$. But from considerations in

earlier chapters, $\eta = 1 - \mathbf{T}/(\mathbf{T} + \delta\mathbf{T}) \approx \delta\mathbf{T}/\mathbf{T}$. We therefore have:

$$\begin{aligned} \frac{\delta\mathbf{p}\Delta\mathbf{V}}{L} &= \frac{\delta\mathbf{T}}{\mathbf{T}} \\ \frac{d\mathbf{p}}{d\mathbf{T}} &= \frac{L}{\mathbf{T}\Delta\mathbf{V}} = \frac{\Delta\mathbf{S}_{\text{pt}}}{\Delta\mathbf{V}} \end{aligned}$$

which is the Clausius-Clapeyron relation. Often the vapour is so much less dense than the solid that $\Delta\mathbf{V} \approx \mathbf{V}_{\text{vapour}}$, which if the pressure is quite low can be approximated using the ideal gas equation as $\mathbf{n}R\mathbf{T}/\mathbf{p}$. We therefore have:

$$\begin{aligned} \frac{d\mathbf{p}}{d\mathbf{T}} &= \frac{L}{\mathbf{n}R\mathbf{T}^2}\mathbf{p} \\ \Rightarrow \mathbf{p}(\mathbf{T}) &\approx p_0 e^{-L/\mathbf{n}R\mathbf{T}} = p_0 e^{-L_m/R\mathbf{T}} \end{aligned}$$

4 Statistical Thermodynamics

Statistical Thermodynamics provides an explanation for the phenomena observed above in terms of what is known about Nature on a microscopic scale – atoms and quantum physics and whatnot.

4.1 Microstates and Macrostates

The *microstate* of a thermal system (such as a gas in a box) is the set of all positions and velocities of the particles it contains (or, from a quantum perspective, the joint wavefunction of all the particles). In other words, the microstate encompasses absolutely all the information that exists about the system at a given moment. According to the *principle of a priori probability*, the system has an equal probability of existing in any of these microstates; this is often justified by the relativistic idea that every point in space (and indeed in velocity space) is equivalent.

The *macrostate* of a system is specified merely by its macroscopic properties, such as \mathbf{p} , \mathbf{T} , etc. A given macrostate will often have an astronomical number of microstates corresponding to it. The system does *not* have an equal probability of existing in any of the macrostates, as some macrostates will have more microstates and therefore are more likely. The number of microstates corresponding to a macrostate of energy E is denoted $\Omega(E)$.

If there are two systems A and B in thermal contact and equilibrium, OLT states that they have the same \mathbf{T} , but this also means that $\Omega_A(E_A)\Omega_B(E_B)$ is maximised, with respect to the constraint that $E_A + E_B = E$, where E is

the total conserved energy. We therefore have:

$$\begin{aligned}\frac{d}{dE_A}(\Omega_A(E_A)\Omega_B(E - E_A)) &= \Omega'_A(E_A)\Omega_B(E_B) - \Omega_A(E_A)\Omega'_B(E_B) = 0 \\ \Rightarrow \frac{\Omega'_A}{\Omega_A} &= \frac{\Omega'_B}{\Omega_B} \\ \Rightarrow \frac{d \ln \Omega_A}{dE_A} &= \frac{d \ln \Omega_B}{dE_B}\end{aligned}$$

Thus the quantity $d \ln \Omega / dE$ must be a function of \mathbf{T} alone; we denote it $\beta(\mathbf{T})$ for now.

We now deduce the relative probability of each microstate of energy E . If a system is known to be in a microstate it has $\Omega_{\text{sys}}(E) = 1$. If this system is connected to a reservoir whose temperature will not change if small amounts of energy are transferred out, it will have $E_{\text{tot}} - E$ energy and $\Omega_{\text{res}}(E_{\text{tot}} - E)$ microstates; this is in fact the total Ω of the overall system as $\Omega_{\text{sys}} = 1$. The ratios of the probabilities that the system will have energy E relative to it having 0 energy is therefore:

$$\begin{aligned}\frac{P(E)}{P(0)} &= \frac{\Omega_{\text{res}}(E_{\text{tot}} - E)}{\Omega_{\text{res}}(E_{\text{tot}})} = \exp \ln \frac{\Omega_{\text{res}}(E_{\text{tot}} - E)}{\Omega_{\text{res}}(E_{\text{tot}})} \\ &= \exp (\ln [\Omega_{\text{res}}(E_{\text{tot}} - E)] - \ln [\Omega_{\text{res}}(E_{\text{tot}})]) \\ &\approx \exp \left(\ln [\Omega_{\text{res}}(E_{\text{tot}})] - E \frac{d \ln \Omega_{\text{res}}}{dE} - \ln [\Omega_{\text{res}}(E_{\text{tot}})] \right) \\ &= \exp(-\beta E)\end{aligned}$$

The probability of the state being in a microstate of energy E is therefore:

$$P(E) = \frac{1}{\mathbf{Z}} e^{-\beta E} \quad \mathbf{Z} = \sum_i e^{-\beta E_i}$$

where \mathbf{Z} is a normalisation constant known as the *partition function*. This is easily adapted to if the system is known to have an energy E but there is some degeneracy so that it could be in any one of $g(E)$ microstates; g is the *degeneracy* of an energy. In this case:

$$P(E) = \frac{1}{\mathbf{Z}} g(E) e^{-\beta E} \quad \mathbf{Z} = \sum_i g(E_i) e^{-\beta E_i}$$

4.2 Internal Energy \mathbf{U}

As one might expect, \mathbf{U} is simply equal to the sum of the energies multiplied by their occupation probabilities; that is:

$$\begin{aligned}\mathbf{U} &= \sum_i P(E_i) E_i = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \\ &= -\frac{1}{\mathbf{Z}} \frac{\partial \mathbf{Z}}{\partial \beta} = \frac{\partial \ln \mathbf{Z}}{\partial \beta}\end{aligned}$$

4.2.1 Equipartition and the form of β

Consider a coordinate $u \in (-\infty, \infty)$, of which the energy is a quadratic function αu^2 , as is seen with kinetic ($u = v$) vibrational ($u = x$) and rotational ($u = \omega$) energies. The internal energy as a result of this coordinate being a degree of freedom is:

$$\begin{aligned}\mathbf{U}_u &= \frac{\int_{-\infty}^{\infty} \alpha u^2 e^{-\beta \alpha u^2} du}{\int_{-\infty}^{\infty} e^{-\beta \alpha u^2} du} \\ &= \frac{\alpha \frac{1}{2} \sqrt{\frac{\pi}{\alpha^3 \beta^3}}}{\sqrt{\frac{\pi}{\alpha \beta}}} \\ &= \frac{1}{2\beta}\end{aligned}$$

which conveniently is independent of α . Furthermore, if the energy is a quadratic function of N coordinates $\{u_i\}$, each with their own value of α , it can be seen that the integral for $\mathbf{U}_{\{u_i\}}$ of all of these coordinates separates cleanly, and we end up with $\mathbf{U}_{\{u_i\}} = N/2\beta$.

Going back to the considerations for a monatomic ideal gas (whose three degrees of freedom are x, y, z), we saw that the internal energy was equal to $\frac{3}{2}k\mathbf{T}$, but we have just shown that for three degrees of freedom the internal energy is $3/2\beta$. This pins down the value of $\beta = 1/k\mathbf{T}$.

4.2.2 Heat Capacities

Now that it is known how β depends on \mathbf{T} , the heat capacity $\partial \mathbf{U} / \partial \mathbf{T}$ of various systems can be deduced. A particularly useful case is the QHO, for which $E_n = (n + 1/2)\hbar\omega$:

$$\mathbf{U} = \frac{\sum_{n=0}^{\infty} (n + 1/2)\hbar\omega e^{-(n+1/2)\hbar\omega/k\mathbf{T}}}{\sum_{n=0}^{\infty} e^{-(n+1/2)\hbar\omega/k\mathbf{T}}} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k\mathbf{T}} - 1}$$

$$\Rightarrow C \equiv \frac{d\mathbf{U}}{d\mathbf{T}} = \frac{\hbar^2 \omega^2}{k\mathbf{T}^2} \frac{e^{\hbar\omega/k\mathbf{T}}}{(e^{\hbar\omega/k\mathbf{T}} - 1)^2}$$

We see that in the high-temperature limit $\mathbf{U} \rightarrow k\mathbf{T}$ and $C \rightarrow k$.

4.3 Entropy \mathbf{S} and the 3rd Law of Thermodynamics

Writing $\mathbf{U} = \sum_i P_i E_i$, we then have:

$$d\mathbf{U} = \underbrace{\sum_i E_i dP_i}_{\delta\mathbf{Q}} + \underbrace{\sum_i P_i dE_i}_{\delta\mathbf{W}}$$

where we have attributed one term to $\delta\mathbf{Q}$ and the other to $\delta\mathbf{W}$ to satisfy the first law. The intuition for these attributions is that when heat is transferred to a system, the energy levels available do not change, but occupation of higher energy levels becomes more probable. Conversely, when work is done on a system, the energy levels change (think about compressing an infinite quantum well, whose energy levels depend on the dimensions). We can thus write a statistical expression for $d\mathbf{S}$:

$$\begin{aligned} d\mathbf{S} &= \frac{1}{\mathbf{T}} \sum_i E_i dP_i \\ &= -\frac{1}{\mathbf{T}} \sum_i k\mathbf{T} (\ln \mathbf{Z} + \ln P_i) dP_i \\ &= -k \ln \mathbf{Z} \underbrace{\sum_i dP_i}_{0 \text{ as } \sum P_i = 1} - k \sum_i \ln P_i dP_i \\ &= -k \sum_i \ln P_i dP_i \\ \Rightarrow \mathbf{S} &= -k \sum_i \int \ln P_i dP_i \\ &= -k \sum_i P_i \ln P_i + k \sum_i P_i + \text{const.} \end{aligned}$$

The integration constant is given by considering $\mathbf{T} = 0$, and the 3rd Law of Thermodynamics, which states:

$$\lim_{\mathbf{T} \rightarrow 0} \mathbf{S} \rightarrow 0$$

Initially, Nernst found that reactions approach $\Delta\mathbf{S} = 0$ as $\mathbf{T} \rightarrow 0$, suggesting that everything at 0K has the same \mathbf{S} (a consequence of this is that it is

impossible to take some gas and bring it to 0K in a finite number of steps). Planck explained this quantum mechanically using the fact that quantum systems have either a unique ground state, or multiple degenerate ground states that are related by a symmetry transformation and so don't really count as different. Either way, the Boltzmann factor $\exp(-E/k\mathbf{T})$ ensures that all particles will be in "the" ground state, and so $P_0 = 1$, $P_{i \neq 0} = 0$. This suggests that at 0K \mathbf{S} is the same for every material etc., and so we may fix it (somewhat arbitrarily) at 0. We thus have:

$$\mathbf{S} = -k \sum_i P_i \ln P_i$$

– the so-called *Gibbs expression* for entropy. In fact, it can be shown that for a given mean, the most likely probability distribution is also given by that which has the largest value of $-\sum P_i \ln P_i$. Indeed, one can even derive the Boltzmann factor by maximising $-\sum P_i \ln P_i$ subject to $\sum P_i = 1$ and $\sum E_i P_i = \bar{E}$.

Technically, this Gibbs expression has been derived for a system in contact with a thermal reservoir, which is always slightly fluctuating. For an *isolated* system, the entropy is not fluctuating at all, which eventually leads to a very slightly different expression. We first convert the sum to an integral over energy:

$$\mathbf{S} = -k \int g(E) P(E) \ln P(E) dE$$

Secondly, we note that very often $g(E)$ rises very rapidly whereas $P(E)$ falls exponentially. As such, their product is usually peaked incredibly sharply – a relative width of $1/\sqrt{N}$ for N molecules. As such, gP is almost 0 except at the energy \bar{E} , the average energy. The entropy is therefore very close to:

$$\mathbf{S} = -k \ln P(\bar{E}) = \frac{\bar{E}}{T} + k \ln \mathbf{Z}$$

Now \mathbf{Z} is given by:

$$\mathbf{Z} = \int g(E) P(E) dE \approx g(\bar{E}) e^{-\bar{E}/k\mathbf{T}} \Delta E$$

where ΔE is very small as the peak is quite sharp. This gives the simple expression:

$$\mathbf{S} = k \ln (g(\bar{E}) \Delta E) \approx k \ln g(\bar{E})$$

An equivalent expression for a discrete set of states (that is, ones which are separated by small but finite amounts; above we considered a continuum of states) is:

$$\mathbf{S} \approx k \ln \Omega_{\max}$$

giving the familiar Boltzmann formula for entropy.

Finally, we relate \mathbf{F} to \mathbf{Z} , from which all the other thermodynamic potentials can be derived (see 2.2.4), so long as the dependence of \mathbf{Z} on \mathbf{V} and \mathbf{T} is known:

$$\begin{aligned}\mathbf{F} &= \mathbf{U} - \mathbf{T}\mathbf{S} = \sum_i (P_i E_i + k\mathbf{T}P_i \ln P_i) \\ &= \sum_i (P_i E_i - P_i E_i - k\mathbf{T}P_i \ln \mathbf{Z}) \\ &= -k\mathbf{T} \ln \mathbf{Z}\end{aligned}$$

5 Radiation

Radiation is analysed slightly differently than gases, because for a gas of photons the number isn't fixed, and the speeds are all the same.

5.1 Radiation Pressure

The *spectral energy density* $u_\lambda(\lambda; \mathbf{T})$ is the energy per unit volume of light of wavelength $\lambda \in (\lambda, \lambda + d\lambda)$.

Aside from λ , u_λ can only depend on temperature; if two connected bodies at the same temperature had different u_λ , energy would flow from one to the other, in violation of 0LT. This leads to the somewhat counter-intuitive phenomenon that an isothermal expansion of a gas of photons has to keep u_λ constant, so more photons are generated.

Let there be $n_E(E) dE$ photons per unit volume with energy $E \in (E, E + dE)$, and assume the angular distribution of their velocities is isotropic. Consider the photons incident on a surface dA in a short time dt , at an angle θ to the normal. The volume of photons which will be incident is $c dt dA \cos \theta$. The proportion of photons which are travelling at an angle $\theta \in (\theta, \theta + d\theta)$ can be shown to be:

$$\frac{d\Omega(\theta)}{4\pi} = \frac{2\pi \sin \theta d\theta}{4\pi} = \frac{1}{2} \sin \theta d\theta$$

Finally, a photon carries momentum $\mathbf{p} = E/c$, so the momentum transferred to the walls (if they are perfectly reflecting) will be $2E \cos \theta/c$; the force $2E \cos \theta/c dt$; and the pressure $2E \cos \theta/c dt dA$. As such, the total radiation pressure is given by:

$$\mathbf{p} = \int \underbrace{n_E(E) dE}_{\text{number per volume}} \underbrace{c dt dA \cos \theta}_{\text{volume at } \theta} \underbrace{\frac{1}{2} \sin \theta d\theta}_{\text{number at } \theta} \underbrace{\frac{2E \cos \theta}{c dt dA}}_{\text{pressure at } E, \theta}$$

$$\begin{aligned}
&= \int_0^\infty E n_E dE \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta \\
&= \frac{1}{3} u(\mathbf{T})
\end{aligned}$$

where $u(\mathbf{T})$ is the total energy per unit volume $= \int_0^\infty u_\lambda d\lambda$. The total number of photons incident per unit area and time (the *flux*) can also be found by these methods:

$$\begin{aligned}
\phi &= \frac{1}{dt dA} \int \underbrace{n_E(E) dE}_{\text{number per volume}} \underbrace{c dt dA \cos \theta}_{\text{volume at } \theta} \underbrace{\frac{1}{2} \sin \theta d\theta}_{\text{number at } \theta} \\
&= \frac{c}{2} \int_0^\infty n_E dE \int_0^{\pi/2} \sin \theta \cos \theta d\theta \\
&= \frac{1}{4} nc
\end{aligned}$$

5.2 Emission and Absorption

The energy hitting a unit area per unit time, in an interval dE , is therefore $E \cdot \frac{1}{4} n_E dE \cdot c = \frac{1}{4} u_E c dE$. The energy per area per time in an interval $d\lambda$ is then $\frac{1}{4} u_\lambda c d\lambda$.

We then define the *spectral absorptivity* $\alpha_\lambda(\lambda)$ as the fraction of photons on $(\lambda, \lambda + d\lambda)$ which are absorbed by the wall. We also define the *spectral radiant exitance* $e_\lambda(\lambda, \mathbf{T})$ as the energy per unit area of photons on $(\lambda, \lambda + d\lambda)$ which are *emitted* by the wall. Taking steady-state (energy in = energy out) for each wavelength range, we obtain:

$$\begin{aligned}
e_\lambda d\lambda &= \alpha_\lambda \frac{1}{4} u_\lambda c d\lambda \\
\Rightarrow \frac{e_\lambda}{\alpha_\lambda} &= \frac{1}{4} u_\lambda c
\end{aligned}$$

which is Kirchhoff's law of thermal radiation.

Black bodies are defined by $\alpha = 1$; they thus have $e_B = \frac{1}{4} u_\lambda c$. Non-black bodies have their spectral radiant exitance defined by $e = \epsilon_\lambda e_B$, where $\epsilon_\lambda(\lambda) < 1$ is the *emissivity*. Combining these results with Kirchhoff's law, we obtain simply:

$$\epsilon_\lambda(\lambda) = \alpha_\lambda(\lambda)$$

5.3 Black-Body Radiation

$$d\mathbf{U} = \mathbf{T} d\mathbf{S} - \mathbf{p} d\mathbf{V} \quad \Rightarrow \quad \left(\frac{\partial \mathbf{U}}{\partial \mathbf{V}} \right)_{\mathbf{T}} = \mathbf{T} \left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}} \right)_{\mathbf{T}} - \mathbf{p}$$

$$\begin{aligned}
\left(\frac{\partial \mathbf{S}}{\partial \mathbf{V}}\right)_{\mathbf{T}} &= \left(\frac{\partial \mathbf{p}}{\partial \mathbf{T}}\right)_{\mathbf{V}} &&= \mathbf{T} \left(\frac{\partial \mathbf{p}}{\partial \mathbf{T}}\right)_{\mathbf{V}} - \mathbf{p} \\
\mathbf{U} = u(\mathbf{T})\mathbf{V}, \quad \mathbf{p} = \frac{1}{3}u &&&\Rightarrow u = \frac{1}{3}\mathbf{T} \frac{du}{d\mathbf{T}} - \frac{1}{3}u \\
\Rightarrow \frac{du}{d\mathbf{T}} &= \frac{4}{\mathbf{T}}u &&\Rightarrow u = A\mathbf{T}^4
\end{aligned}$$

A is an unknown constant of integration, but we at least have the temperature dependence. We can thus deduce the emission from a black body, given that we deduced $e_B = \frac{1}{4}u_\lambda c$ earlier. The total emission per area per time is therefore:

$$\int e_\lambda d\lambda = \int \frac{1}{4}u_\lambda c d\lambda = \frac{1}{4}cu = \sigma \mathbf{T}^4$$

where σ is another constant. We can actually derive the value of this, in a similar way as is done in the Condensed Matter course by considering the number of available quantum states. Consider a cube of side length L ; the \mathbf{k} states available are:

$$\frac{\pi}{L}(n_x, n_y, n_z)$$

for a set of three positive integers. These states are uniformly distributed in \mathbf{k} -space, and each take up a \mathbf{k} -volume of π^3/\mathbf{V} , as $\mathbf{V} = L^3$. Taking into account the two possible polarisation directions for a photon with a particular value of \mathbf{k} , the number of photon states between $|\mathbf{k}|$ and $|\mathbf{k}| + \delta k$ is:

$$\delta \mathbf{N} = 2 \frac{4\pi k^2 \delta k}{8} \frac{\mathbf{V}}{\pi^3} = \frac{\mathbf{V}k^2}{\pi^2} \delta k \Rightarrow g(k) = \frac{\mathbf{V}k^2}{\pi^2}$$

Using the fact that $E = \hbar\omega = \hbar ck$ and $k = 2\pi/\lambda$, we can obtain the density of energy states $g(E)$ and $g(\lambda)$ also:

$$g(E) = \frac{\mathbf{V}E^2}{\hbar^3 c^3 \pi^2} \quad g(\lambda) = \frac{8\pi \mathbf{V}}{\lambda^4}$$

Now from a classical point of view, photons have two quadratic variables in which they store energy: the electric field and magnetic field ($\frac{1}{2}\epsilon_0 E^2$ and $\frac{1}{2}\mu_0 H^2$), and so would be given an energy $k\mathbf{T}$ each (try to avoid confusing k , the constant, with k , the magnitude of the wavevector; forgive me for not putting subscripts everywhere). This would lead to $u_\lambda = 8\pi \mathbf{V} k \mathbf{T} / \lambda^4$, the Rayleigh-Jeans Law, but this is catastrophically wrong at low λ .

Planck proposed that each mode can have only an integer number of photons in it, each with discrete energy $\hbar\omega$, which gives a mean energy of a mode of frequency ω of:

$$\bar{U}(\omega; \mathbf{T}) = \frac{\sum_0^\infty n \hbar \omega e^{-\beta \hbar \omega}}{\sum_0^\infty e^{-\beta \hbar \omega}} = \frac{\hbar \omega}{e^{\hbar \omega / k \mathbf{T}} - 1}$$

Now the spectral energy density (as a function of ω rather than λ) is found using the expression for $g(E)$ above:

$$\begin{aligned} u_\omega(\omega; \mathbf{T}) &= g(\omega) \bar{U}(\omega; \mathbf{T}) / \mathbf{V} = \frac{g(E) \delta E}{\mathbf{V}} \frac{\hbar\omega}{\delta\omega e^{\hbar\omega/k\mathbf{T}} - 1} = \frac{\mathbf{V}(\hbar\omega)^2}{\mathbf{V}\hbar^3 c^3 \pi^2} \hbar \frac{\hbar\omega}{e^{\hbar\omega/k\mathbf{T}} - 1} \\ &= \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\hbar\omega/k\mathbf{T}} - 1)} \end{aligned}$$

– the Planck black-body spectrum. This can instead be written in terms of λ :

$$u_\lambda(\lambda; \mathbf{T}) = \frac{8\pi ch}{\lambda^5 (e^{hc/\lambda k\mathbf{T}} - 1)} = \lambda^{-5} f(\lambda\mathbf{T})$$

When one tries to find the wavelength for which u_λ is at its peak, one obtains a transcendental equation for $\lambda_{\max} \mathbf{T}$, with the solution

$$\lambda_{\max} \mathbf{T} \approx 2.9\text{mm K}$$

known as *Wien's displacement law*.

Integrating u_ω over ω , we obtain the *full* energy density as:

$$u(\mathbf{T}) = \frac{\pi^2 k^4}{15 \hbar^3 c^3} \mathbf{T}^4$$

which is not only proportional to \mathbf{T}^4 , but also gives the value of A from earlier. Similarly, the power flux from a black-body is now found to be:

$$\frac{\pi^2 k^4}{60 \hbar^3 c^2} \mathbf{T}^4$$

fixing the constant σ to a memorable 5.67e8 watts per square metre.

6 Properties of gases

6.1 The Maxwell-Boltzmann Distribution

Consider a dilute monatomic gas, with $E = \frac{1}{2}mv^2$. Particles can exchange energy by colliding; each particle is like a tiny system, with the rest of the gas as a reservoir at temperature \mathbf{T} . As such, we can apply the Boltzmann distribution, but we must still be careful. The microstates of equal probability are those with a velocity in the range $(\mathbf{v}, \mathbf{v} + d\mathbf{v})$, and so we have that the velocity distribution varies as:

$$f(\mathbf{v}) \propto e^{-mv^2/k\mathbf{T}}$$

which is a Gaussian centred on the origin – the most likely velocity of a gas molecule is that it is stationary! This is counter-intuitive because our intuition thinks more in terms of speed v than velocity \mathbf{v} . There are a large number of \mathbf{v} -states with a speed on $(v, v + dv)$, in fact the number grows as v^2 as the volume of a thin spherical shell of radius v and thickness dv is $4\pi v^2 dv$:

$$f(v) \propto v^2 e^{-mv^2/k\mathbf{T}}$$

This is the *Maxwell-Boltzmann distribution*. It can be easily normalised provided that one knows that $\int_0^\infty u^2 e^{-\alpha u^2} du = \frac{1}{4} \sqrt{\frac{\pi}{\alpha^3}}$:

$$f(v) = \left(\frac{m}{2\pi k\mathbf{T}} \right)^{3/2} \cdot 4\pi v^2 \cdot e^{-mv^2/2k\mathbf{T}}$$

From this, we can obtain, in size order:

$$v_{\text{mp}} = \sqrt{\frac{2k\mathbf{T}}{m}} \quad \langle v \rangle = \sqrt{\frac{8k\mathbf{T}}{\pi m}} \quad v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k\mathbf{T}}{m}}$$

The final result could be anticipated by noting that the mean kinetic energy is $\frac{3}{2}k\mathbf{T} = \frac{1}{2}m \langle v^2 \rangle$.

This distribution can also be used to rederive the ideal gas law. The number of particles per unit with speed on $(v, v + dv)$ approaching a wall at an angle on $(\theta, \theta + d\theta)$ is:

$$nf(v) dv \cdot \frac{1}{2} \sin \theta d\theta$$

The number which will be inbound on an area dA in a time dt is:

$$nf(v) dv \cdot \frac{1}{2} \sin \theta d\theta \cdot v \cos \theta dA dt$$

These will transfer momentum $2mv \cos \theta$ each, so the average pressure is:

$$\begin{aligned} \mathbf{p} &= \int nf(v) dv \cdot \frac{1}{2} \sin \theta d\theta \cdot v \cos \theta dA dt \cdot \frac{2mv \cos \theta}{dt dA} \\ &= nm \int_0^\infty v^2 f(v) dv \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta \\ &= \frac{1}{3} nm \langle v^2 \rangle = nk\mathbf{T} \end{aligned}$$

note that here n is the number of particles per unit volume (not to be confused with \mathbf{n} which is green) and so this does indeed agree with the ideal gas law.

Finally, we mention *Dalton's Law* – the total pressure is equal to the sum of the *partial pressures* of all the species present; the partial pressure of a species is the pressure that would be exerted if that species alone were present. Phrased mathematically:

$$\mathbf{p} = k\mathbf{T} \sum_i n_i = \sum_i \mathbf{p}_i$$

6.2 Effusion

Effusion is where molecules of a gas pass through a very small hole – the molecule “goes through in one go”. This should be contrasted with *diffusion*, whereby particles gradually bumble over.

The particle flux (in $\text{m}^{-2} \text{s}^{-1}$) is given by the integral:

$$\begin{aligned} \Phi &= \frac{1}{dA dt} \int n f(v) dv \cdot dA v dt \cos \theta \cdot \frac{1}{2} \sin \theta d\theta \\ &= \frac{1}{2} n \int_0^\infty v f(v) dv \int_0^{\pi/2} \sin \theta \cos \theta d\theta \\ &= \frac{1}{4} n \langle v \rangle \end{aligned}$$

For an ideal gas obeying the Maxwell-Boltzmann distribution, $\langle v \rangle = \sqrt{8k\mathbf{T}/\pi m}$ and $n = \mathbf{p}/k\mathbf{T}$, and so:

$$\Phi = \frac{\mathbf{p}}{\sqrt{2\pi k\mathbf{T}m}}$$

The effusion rate out of a hole of area dA is then clearly given by ΦdA . The *Knudsen method* uses this principle to determine the vapour pressure of a liquid with total mass M :

$$\frac{dM}{dt} = -m\Phi dA = -\mathbf{p} dA \sqrt{\frac{m}{2\pi k\mathbf{T}}} \Rightarrow \mathbf{p} = -\frac{1}{dA} \sqrt{\frac{2\pi k\mathbf{T}}{m}} \frac{dM}{dt}$$

It is important to note that these effusing molecules do *not* have a Maxwell-Boltzmann distribution. The number of molecules with speed on $(v, v + dv)$ is proportional to $v f(v) \propto v^3 e^{-mv^2/2k\mathbf{T}}$; there is an extra factor of v .

6.3 Mean Free Path

Molecules in a gas are constantly colliding with each other; in a dilute gas these collisions can be treated classically. As a molecule moves through space, there is a certain volume in which if there are any other molecules a collision

will take place. If a molecule is moving at a speed v , then in a time dt it will sweep through a prism (usually a cylinder) of volume $\sigma v dt$, where σ , the collision cross-section, is the cross-sectional area of this prism. For two different hard spheres, this area is given by:

$$\sigma = \pi(a_1 + a_2)^2$$

for a single gas this simplifies to πd^2 ; note that this uses the *diameter*, not the radius.

If there are n other particles per unit volume, then in a time dt the moving molecule will hit an average of $n\sigma v_r dt$ particles, where v_r is the *relative* velocity of the two. The molecule therefore hits $n\sigma v$ particles per unit time, and so the mean time between collisions is

$$\tau = \frac{1}{n\sigma \langle v_r \rangle}$$

The *mean free path* is therefore given by:

$$\lambda = \langle v \rangle \tau = \frac{\langle v \rangle}{n\sigma \langle v_r \rangle}$$

Now we require an expression for $\langle v_r \rangle$. Consider two molecules moving at velocities \mathbf{v}_1 and \mathbf{v}_2 . Then $\mathbf{v}_r = \mathbf{v}_2 - \mathbf{v}_1$, and then:

$$\begin{aligned} \langle v_r^2 \rangle &= \langle v_2^2 \rangle + \langle v_1^2 \rangle - \underbrace{2 \langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle}_0 \\ &= 2 \langle v^2 \rangle \\ \Rightarrow \langle v_r \rangle &\approx \sqrt{\langle v_r^2 \rangle} = \sqrt{2} \langle v \rangle \end{aligned}$$

The approximations are justified in the fact that the difference between $\langle v \rangle$ and v_{rms} are quite close together for a MB distribution. We therefore have:

$$\lambda = \frac{1}{\sqrt{2}n\sigma} = \frac{k\mathbf{T}}{\sqrt{2}\mathbf{p}\sigma}$$

6.4 Viscosity η

Viscosity of a fluid causes a velocity gradient $d \langle v_x \rangle / dz$ to be created between two plates, one of which is being pushed along by a force F . When a molecule moves from height z to $z + dz$, it goes from a speed $\langle v_x \rangle(z)$ to $\langle v_x \rangle(z) + \frac{d \langle v_x \rangle}{dz} dz$, and so gains momentum $m \frac{d \langle v_x \rangle}{dz} dz$, which is provided by the force.

Consider molecules travelling at an angle θ to the vertical z -axis. On average, then, $dz = \lambda \cos \theta$. The number travelling upwards on $(\theta, \theta + d\theta)$ and $(v, v + dv)$ across an area dA in a time dt is:

$$nf(v) dv \cdot \frac{1}{2} \sin \theta d\theta \cdot v \cos \theta dA dt$$

Thus the momentum transfer over this area and time is:

$$\begin{aligned} \mathbf{p} &= \int nf(v) dv \cdot \frac{1}{2} \sin \theta d\theta \cdot v \cos \theta dA dt \cdot m \frac{d\langle v_x \rangle}{dz} \cdot \lambda \cos \theta \\ &= \frac{1}{2} nm \lambda \frac{d\langle v_x \rangle}{dz} dA dt \int_0^\infty v f(v) dv \int_0^\pi \cos^2 \theta \sin \theta d\theta \end{aligned}$$

[where the θ integration goes from 0 to π to account for molecules moving the other way]

$$= \frac{1}{3} nm \lambda \langle v \rangle \frac{d\langle v_x \rangle}{dz} dA dt$$

The viscosity is defined by:

$$\frac{F}{dA} = \eta \frac{d\langle v_x \rangle}{dz}$$

and given that $F/dA = \mathbf{p}/dA dt$, we have:

$$\begin{aligned} \eta &= \frac{1}{3} nm \lambda \langle v \rangle = \frac{1}{3} \frac{\mathbf{p}}{k\mathbf{T}} m \frac{k\mathbf{T}}{\sqrt{2}\mathbf{p}\sigma} \sqrt{\frac{8k\mathbf{T}}{\pi m}} \\ &= \frac{2}{3\sigma} \sqrt{\frac{k\mathbf{T}m}{\pi}} \end{aligned}$$

We see that this expression is proportional to $\mathbf{T}^{1/2}, m^{1/2}, d^{-2}, n^0$.

6.5 Thermal Conductivity κ

When a molecule moves from height z to $z + dz$, it moves from a temperature $\mathbf{T}(z)$ to $\mathbf{T}(z) - \nabla \mathbf{T} dz$, assuming the temperature gradient is directed towards $-z$. Anyway, the molecule then dissipates its “excess energy” $C^* \nabla \mathbf{T} dz$, where C^* is the specific heat of a single molecule, as heat.

Again $dz = \lambda \cos \theta$. Using the expression above for the number of molecules travelling upwards at a certain velocity and angle, the total heat transferred is:

$$\mathbf{Q} = \int nf(v) dv \cdot \frac{1}{2} \sin \theta d\theta \cdot v \cos \theta dA dt \cdot C^* \nabla \mathbf{T} \cdot \lambda \cos \theta$$

$$\begin{aligned}
&= \frac{1}{2} n C^* \lambda \nabla \mathbf{T} \, dA \, dt \int_0^\infty v f(v) \, dv \int_0^\pi \cos^2 \theta \sin \theta \, d\theta \\
&= \frac{1}{3} n C^* \lambda \langle v \rangle \nabla \mathbf{T} \, dA \, dt
\end{aligned}$$

The thermal conductivity is defined (being lax about vectors and magnitudes) by:

$$J = \kappa \nabla \mathbf{T}$$

where $J = \mathbf{Q} / dA \, dt$. We can thus identify:

$$\begin{aligned}
\kappa &= \frac{1}{3} n C^* \lambda \langle v \rangle = \frac{1}{3} C_V \lambda \langle v \rangle \\
&= \frac{2 C_V}{3 \sigma} \sqrt{\frac{k \mathbf{T}}{\pi m}}
\end{aligned}$$

which we see is proportional to $\mathbf{T}^{1/2}, m^{-1/2}, d^{-2}, n^0$, all of which except m are the same dependence as η .

6.6 Self-Diffusion Coefficient D

Let $n^*(z)$ be the concentration of some starred molecules of interest. The number of excess molecules coming from a height z to a height $z + dz$ is:

$$\begin{aligned}
&\int f(v) \, dv \cdot \frac{1}{2} \sin \theta \, d\theta \cdot v \cos \theta \, dA \, dt \cdot \nabla n^* \cdot \lambda \cos \theta \\
&= \frac{1}{2} \lambda \nabla n^* \, dA \, dt \int_0^\infty v f(v) \, dv \int_0^\pi \cos^2 \theta \sin \theta \, d\theta \\
&= \frac{1}{3} \lambda \langle v \rangle \nabla n^* \, dA \, dt
\end{aligned}$$

The self-diffusion coefficient is defined by:

$$\Phi = D \nabla n^*$$

where Φ is the number of particles per unit area per unit time. Thus:

$$\begin{aligned}
D &= \frac{1}{3} \lambda \langle v \rangle = \frac{1}{3} \frac{k \mathbf{T}}{\sqrt{2} \mathbf{p} \sigma} \sqrt{\frac{8 k \mathbf{T}}{\pi m}} \\
&= \frac{2}{3 \mathbf{p} \sigma} \sqrt{\frac{k^3 \mathbf{T}^3}{\pi m}}
\end{aligned}$$

which is in fact proportional to $\mathbf{T}^{3/2}, m^{-1/2}, d^{-2}, n^{-1}, \mathbf{p}^{-1}$.