1 Introduction

This module has two types of material in it:

1. Using simple models to deduce microscopic quantities from macroscopic ones (e.g. the calculation of the size of atoms in next section). Or vice versa.

2. Setting up thermodynamics at the level of the zeroth and first laws (second and third next year). This is all about relationships between macroscopic variables – eg the pressure, p, volume, V, and temperature, T, of a gas with no microscopic information needed. And towards the end of the module, we will make contact with some microscopic foundations for thermodynamics.

1.1 Phases of matter

The phases of water are very familiar: water, steam and ice. The everyday experience of steam being "hot" and ice "cold" can be quantitatively represented in the phase diagram of water Fig. (1.1)
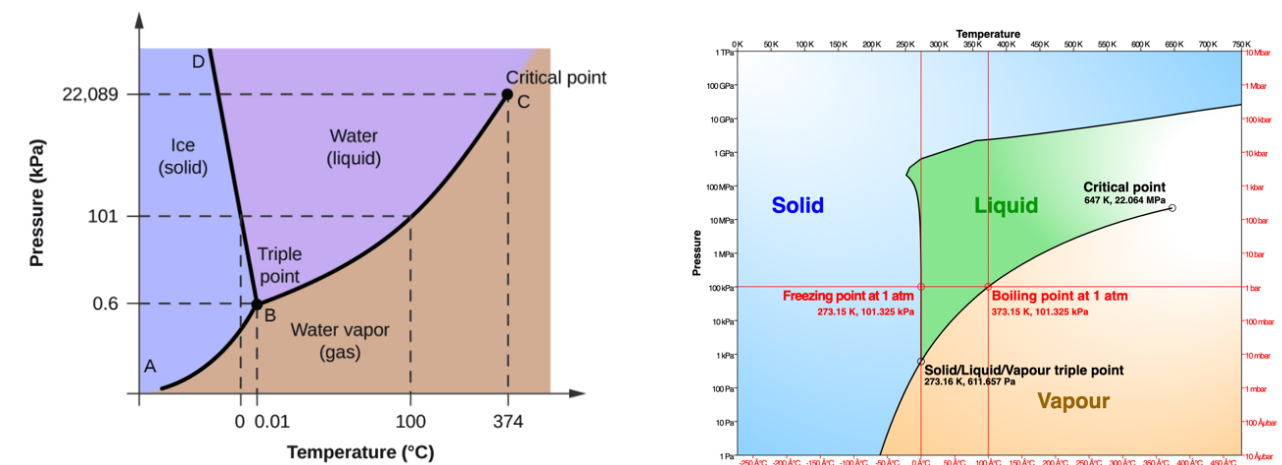

Figure 1.1: Left: A conventional phase diagram of water; Right: with a logarithmic pressure scale.

Consider the left hand figure in Fig. (1.1). Atmospheric pressure is 10^5 Pa. If one follows the horizontal line corresponding to that pressure you see the conventional ordering with respect to temperature of ice then water then steam, with the boundaries between the phases at the familiar temperatures: $0°$C and $100°$C.

Away from atmospheric pressure some less familiar phenomena are represented.

Below pressures of 0.6 kPa, we see there is no liquid phase: upon heating ice it transforms ("sublimates") into steam directly. (This happens with CO_2 at atmospheric pressure, hence the name "dry ice" see the phase diagram of CO_2, A.S. Witkowski et al *Arch. Therm.* **35,** 117 (2014).

And the solid-liquid boundary moves to lower temperatures as pressure is increased away from atmospheric pressure. This may be one reason why ice-skates work – by melting the ice underneath them by pressure forming a lubricating film. (A analysis is in *Why is Ice slippery?, Physics today,* **58,** 50, (2005). Ice is unusual in this attribute, most melting curves, $p_{\mathrm{m}}(T)$, have a positive gradient, related to the density of ice being lower than water (if this were not true the Titanic would still be afloat).

In the right hand figure in Fig. (1.1) the many different phases of ice (due to different crystal structures) at elevated pressures are missing. They may be seen in this figure, where they are denoted by upper case roman numerals.

Terrestrial ice sheets are not thick enough (at least currently) to reach the "next" phase of ice, Ice IX. The pressure at the bottom of the deepest (5 km) Antarctic ice sheet is around 500 Atm or 5×10^7 Pa.
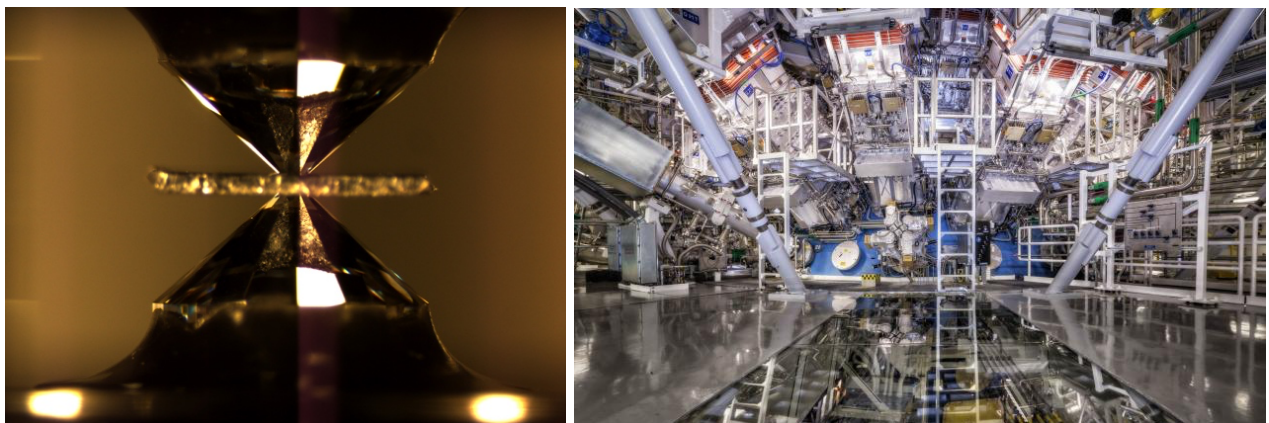

Figure 1.2: Left: a diamond anvil cell (credit: Carleton College) ; right: the National Ignition Facility target (credit: NIF).

The pressure in the logarithmic, righthand figure Fig. (1.1), goes up to 1 TPa $\simeq 10^7$ Atm. This is not relevant for ice on Earth, but is relevant for other materials in geophysics and astrophysics. Examples being: the pressure at the centre of the Earth is around 0.365 TPa; and at the centre of Jupiter and Saturn is around 5 TPa; and the centre of the Sun is beleived to be around 26 PPa (petaPascal) $\simeq 26 \times 10^{10}$ Atm. The centre of Jupiter has a mysteriously small core, only discovered recently.

The high pressure "frontier" in small laboratory experiments is around a TPa, so approaching the pressure of the centres of the giant planets. The small and more delicately controlled environment of a diamond anvil cell (left hand figure in Fig. (1.2)), where two diamonds are pushed together with the sample in between, can achieve 400 GPa, with a new design

approaching 1 TPa.

For higher pressures, the much larger National Ignition Facility (see the righthand figure in Fig. (1.2)) in the California will provide pressures up to 10^4 TPa, and hence laboratory astrophysics. This works by providing pressure from 192 (very large) lasers focused on the same point.

Finally maybe it is worth noting that atmospheric pressure, 10^5 Pa, is not that small. Compare it with the pressure under a skate supporting a 50 kg person. Let us assume the skate has a width 1 cm and a length 20 cm. Then the total surface area of two such skates is 40 cm^2, and the pressure is

$$p = \frac{50 \times g}{4 \times 10^{-3}} \, \text{N m}^{-2} = 1.25 \times 10^5 \, \text{Pa} \, ,$$

which is roughly atmospheric pressure, but one would not wish to place one's finger under the skate!

1.2 Not all phases are gases, liquids and solids

We experience one everyday: the Sun. Although the Sun is gaseous, all the atoms except in its outer regions are ionised. Thus it is an electrically conducting gas, a *plasma*. In many situations one may regard the conductivity as being very high, or infinite, and that aspect is a contributory ingredient in the formation of sun spots and the precursors of coronal mass ejections.

Some other phases are due to quantum mechanics. The superfluid phase of helium is a quantum liquid, and the ultracold gases which exhibit Bose-Einstein condensation into a single quantum state are quantum gases, with many phenomena distinct to the familiar classical ones.

And there are transitions associated with the electrons in solid: magnetism (of which the magnetism in a bar magnet is the simplest of many possibilities), superconductivity and stranger things – charge- and spin-density waves …

Even under ambient conditions, there are anomalies. A familiar one is that there are *allotropes* of elemental carbon: it may be diamond or graphite (or nanotubes or buckyballs of C$_{60}$). Diamond is one of the hardest substances known, but graphite shears very easily (why one can make pencils with it) Fig. (1.3). The other physical properties of these are also very different: diamond is a very bad electrical conductor (but the best thermal conductor), graphite conducts, but is very anisotropic because of its layered crystal structure, with a solitary layer being graphene.

Less familiar is that there two types of liquid Sulphur – one is a liquid of rings the other being
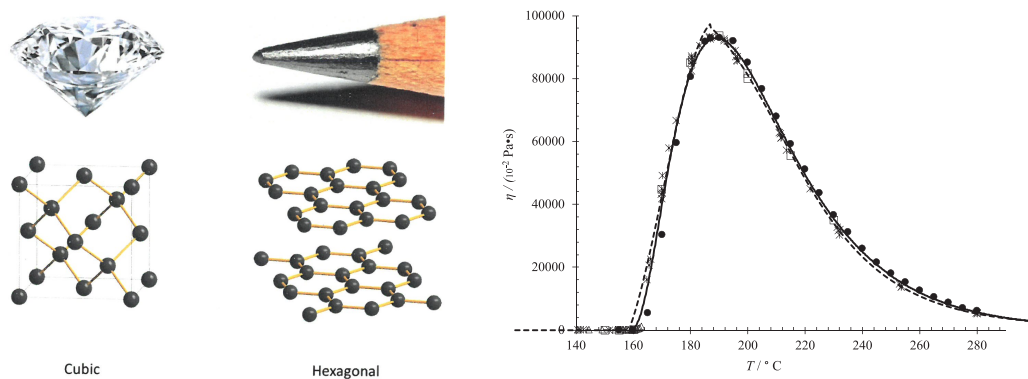
Figure 1.3: Left: Two allotropes of carbon, with very different properties; **Right**: the vicosity of liquid sulphur through the ring-polymer transition temperature, as reflected by the viscosity. *Credit* G.O. Sofekun et al *J. Rheol.* **62** 469 (2018).

a liquid of polymers both existing at around room temperature. The viscosity of the latter is much higher as the chains become entangled Fig. (1.3). Similar transitions occur in other elemental liquids at high pressure, eg Phosphorus (Y. Katayama et al . *Nature,* **403**, 170 (2000).

Liquid crystals sounds like an oxymoron, but they are made of molecules and not atoms. The molecules orient in the same direction ("crystalline") although the molecular centres of mass remain disordered and "liquid". The simplest type are *nematics*, but there are more exotic varieties. They are used in soap, bullet proof vests and puncture-proof bicycle tyres (kevlar is a liquid crystal polymer) and television screens.

The last two classes of examples are really just adding extra variables to a liquid phase. Worse things can happen – one cannot find an appropriate label for a "phase".

Dry sand is an example – it can flow like a liquid (eg egg-timer), but *not quite* like a liquid. It flows at same rate independent of the amount of sand in the upper chamber (which is why it is useful as a timer), here is an article on sand flow. A liquid would flow faster if there were a bigger pressure head.

On the other hand you can stand on sand – you do not sink more than a few centimetres, unlike a liquid. And the beach is not flat even if there is no wind. Compare the ocean.

So it cannot be classified, although *moist* sand is more like a normal solid. Quicksand is still more complicated.

The flow of sand and other *granular* media (eg gravel, talcum powder, rice, grain in a silo, avalanches, landslides ...) is still not well understood – even at the level of the equations of

motion (let alone their solution). Experiments to understand these media are taking place here in the Positron Emission Centre in the Medical Physics building in collaboration with the chemical engineers.

2   Bibliography

The books which are closest to the level of the module in the properties of matter treatment are:

Properties of matter B. H. Flowers, E. Mendoza, wiley (1970)

and

Understanding the properties of matter, Second Edition, Michael De Podesta, CRC Press (2020). ebook, and hardcopy *Understanding the properties of matter*, Second Edition, Michael De Podesta, CRC Press (2020).

Slightly higher level is the ebook (which you can download in its entirety)

Gases, liquids, and solids : and other states of matter D. Tabor, CUP (1991). and hardcopy: *Gases, liquids, and solids : and other states of matter* D. Tabor, CUP (1991).

For thermodynamics books which will be useful next year and indeed later are the ebook:

Statistical physics, second edition, F. Mandl, Wiley (1988) and hardcopy: *Statistical physics*, second edition, F. Mandl, Wiley (1988)

Elements of classical thermodynamics for advanced students of physics. A. B. Pippard (Alfred Brian), 1920- CUP (1957) possibly the most beautiful book on thermodynamics.

For elasticity (rather more than is needed), the ebook

Introduction to the physics of fluids and solids, James S. Trefil, Dover (2009) and hard copy *Introduction to the physics of fluids and solids*, James S. Trefil, Pergamon (1975)

The authors are depicted in Fig. (2.1)

Figure 2.1: The authors: Brian Flowers, David Goodstein, Franz Mandl, Eric Mendoza, Brian Pippard, Michael de Podesta, David Tabor and James Trefil.