

Fri: HW 1 by Spm

~~SPM~~

Tues: Read 2.22, 2.6, 2.7

Thermodynamic states: gas

Consider any gas. We can describe the state of the gas using the following bulk variables (we might add more later):

N = number of gas particles

V = volume of gas

P = pressure of gas

T = temperature of gas

In "equilibrium" thermodynamics the system must be such that each variable only assumes one value for the entire system. Thus the pressure must be the same throughout the gas. Similarly the temperature must be the same throughout the gas. So

An equilibrium state is one for which each variable assumes one value for the entire system.

Demo: PhET Gas Prop (old version)

- add 200 - watch pressure vary + eventually reach equilib.
- compress rapidly - no true pressure value.

Demo: PSU-5 Free Expansion of Gas

The classical thermodynamics that we will consider only concerns equilibrium states and changes from one equilibrium state to another.

A system in a thermal equilibrium state is often described as being in thermal equilibrium.

Thermodynamic states: other systems

The statements made so far for a gas have analogous versions for any other system. In general

List variables that describe state of system.

A thermal equilibrium state is one for which each variable takes one value throughout the system

Eg. Nuclear spins
 N = number spins
 \vec{M} = bulk magnetization
 T = temperature

Example
 $N = 10^{20}$
 $\vec{M} = 60 \text{ Am}^2 \hat{z}$
 $T = 500 \text{ K}$

e.g. $N = 10^{20}$
 $\vec{M} = 60 \text{ Am}^2$
 $T = 500 \text{ K}$

Then the science of thermodynamics involves:

- 1) relating these variables to each other for thermal equilibrium states and describe how one can deduce these from experiment
- 2) describing processes in which a system changes from one equilibrium state to another.
- 3) describing energy flow in thermodynamic processes in terms of variables
- 4) describing entropy changes in terms of variables

Temperature

Again consider a gas. Some of the variables used to describe the state of the system have definitions that stem from geometrical or classical mechanical considerations.

Volume can be calculated geometrically and pressure via force per unit area. What about temperature? How can temperature be defined?

We aim for a definition that avoids

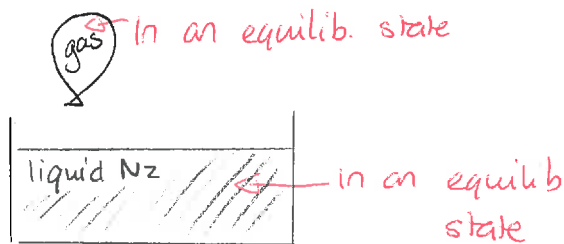
- 1) relying on human sensation
- 2) relying on a particular apparatus.

Eventually we will arrive at a mathematical derivation of temperature that involves entropy. More immediately we aim for a more intuitive definition.

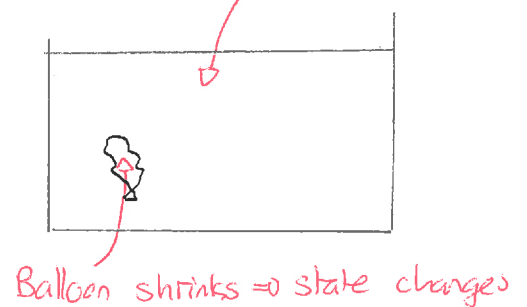
The immediate definition will involve interacting systems and the notion of equilibrium between these systems. Consider the following example:

Example * A balloon holds a gas at room temperature **System A**
* A pool of liquid nitrogen is at the boiling point of liquid nitrogen **System B**

Initially - systems are separated and isolated from each other



Later - systems are in contact



Once they are in contact, there are observable changes in the states of the system. Because their states changed observably we say that they were not in thermal equilibrium with each other.

Eventually there will no longer be any observable changes for the two systems and we then say that they are in thermal equilibrium with each other. ■

In general

Systems A and B are in thermal equilibrium if, once they are placed in thermal contact with each other their states do not change observably

We will then state:

Systems A and B are at the same temperature
 \Leftrightarrow Systems A and B are in thermal equilibrium with each other.

This is an initial attempt at defining temperature. To be logically consistent, it requires a general empirical observation, the zeroth law of thermodynamics.

This states:

If systems A and B are in thermal equilibrium with each other and systems A and C are in thermal equilibrium with each other then systems B and C are also in thermal equilibrium with each other.

Example: Consider three objects:

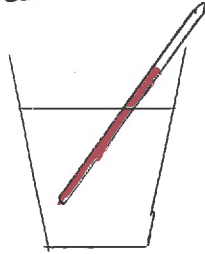
A \equiv small thermometer

B \equiv water

C \equiv alcohol

Two operations plus zeroeth law

① Place A in B



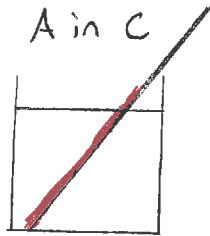
\rightarrow observe large change in A
negligible change in B

\rightarrow eventually no more changes

\Rightarrow A in equilibrium with B.

(A, B have same temp)

② Place A in C



\rightarrow observe no change in either

\Rightarrow A in equilibrium with C

(A, C have same temp)

③ Zeroeth law \Rightarrow B, C are in equilibrium

(B, C have same temperature). \square

The zeroeth law sorts objects into categories with all objects in a single category in thermal equilibrium with each other. These objects all have the same temperature. We can then make a preliminary definition of temperature:

Two systems have the same temperature if they are in thermal equilibrium with each other. Two systems have different temperatures if they are not in thermal equilibrium with each other.

In order to assign numbers to temperatures and devise a temperature scale one has to use a physical device which offers observable changes when subjected to different temperatures. A historically useful example of such a device is the gas thermometer. This indicates an absolute zero of temperature.

The result scale is called the Kelvin (K) scale.

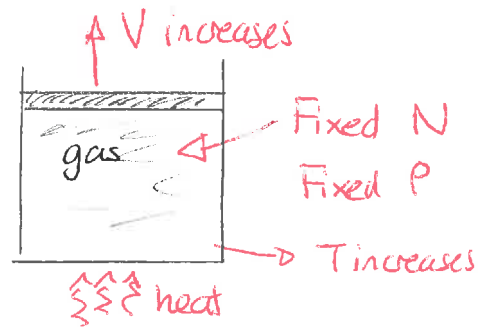
Equations of state 2.5

Consider a gas whose state can be described by four variables:

$$N, V, T, P$$

Empirical observations indicate that these are not all independent.

For example keeping a gas at fixed pressure and raising its temperature by a certain amount will raise the volume by a well-defined amount that depends on the change in pressure.



Thus:

For a gas N, V, T, P are not all independent

These variables are therefore related by an equation, called the equation of state. The nature of the equation depends on the type of gas.

i) Ideal gas

For a sufficiently dilute gas, the variables are related by

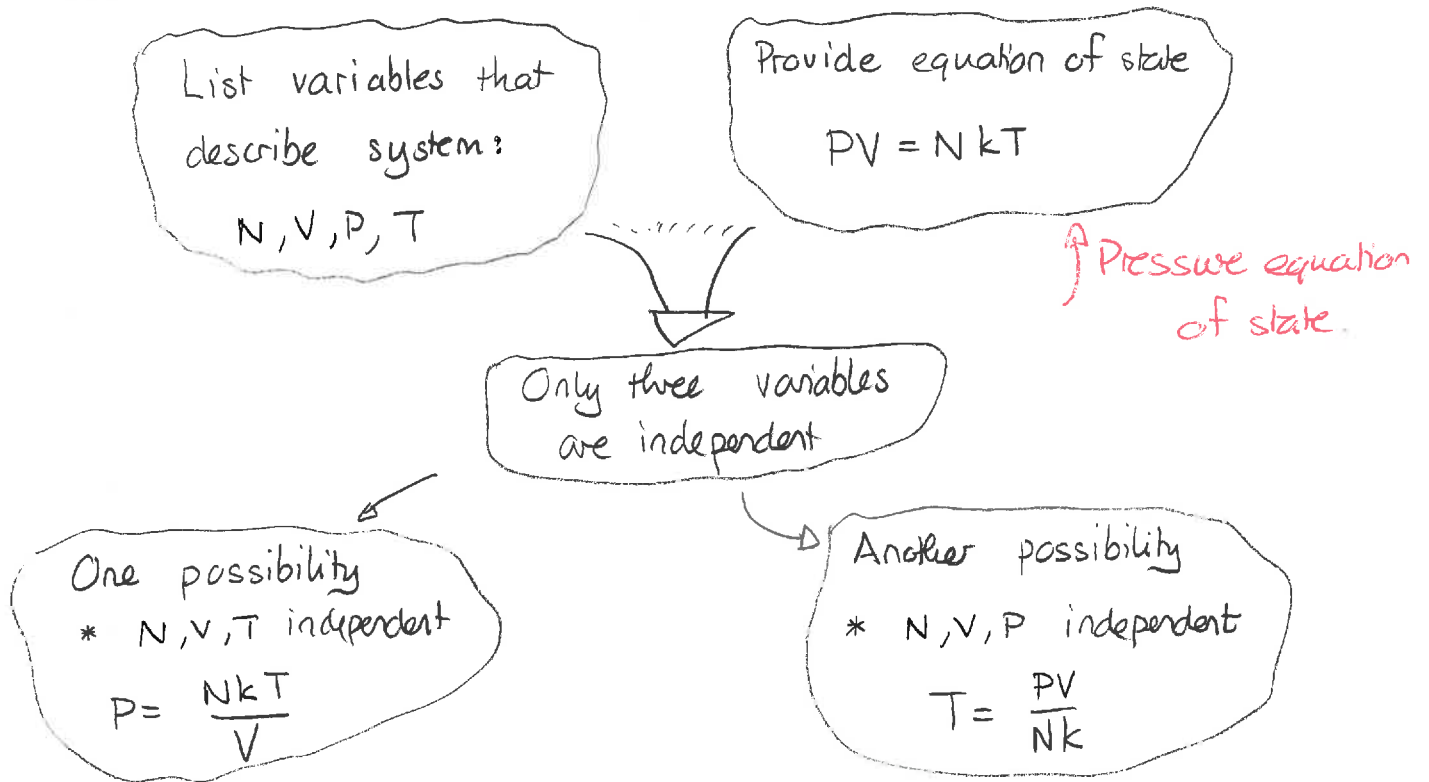
$$PV = NkT$$

where $k = 1.38 \times 10^{-23} \text{ J/K}$ is Boltzmann's constant. This is called the ideal gas law. The temperature must be in Kelvin.

Any gas that obeys the ideal gas law is called an ideal gas.

Given a single equation that relates four variables we have some choice in which three are regarded as independent and which single variable is dependent.

The scheme is:



We will see later that it will be important for mathematical reasons to specify which variables are independent.

2) Von der Waals gas

Real gases differ from ideal gases by:

- there will be attractive interactions between molecules
- each molecule occupies a certain volume in space.

A more sophisticated model that partly accounts for these is the van der Waals model, for which the equation of state is:

$$\left(P + \frac{N^2}{V^2} a\right)(V - Nb) = NkT$$

where a, b are constants. These depend on the particular gas although we need $V - Nb > 0$.

1 Equations of state

Consider various gases for which the number of gas molecules is fixed and the volume of the gas is fixed. In each case the temperature changes by a factor of three.

- Suppose that the gas is an ideal gas. By what factor does the pressure change?
- Suppose that the gas is a van der Waals gas, with $a > 0$. Does the pressure change by a factor of three, a factor of more than three or a factor of less than three?

Answer: a) $PV = NkT$

$$P = \frac{NkT}{V} = \frac{Nk}{V} T$$

If $T \rightarrow 3T$ then $P \rightarrow 3P$.

b) $\left(P + \frac{N^2}{V^2} a\right)(V - Nb) = NkT$

$$\Rightarrow P + \frac{N^2}{V^2} a = \frac{Nk}{V - Nb} T$$

$$\Rightarrow P = \underbrace{\frac{Nk}{V - Nb} T}_{\text{triples}} - \underbrace{\frac{N^2}{V^2} a}_{\text{stays const}} \Rightarrow P \text{ increases}$$

Now $P_i = \frac{Nk}{V - Nb} T_i - \frac{N^2}{V^2} a \Rightarrow \frac{Nk}{V - Nb} T_i = P_i + \frac{N^2}{V^2} a$

$$P_f = \frac{Nk}{V - Nb} T_f - \frac{N^2}{V^2} a$$

$$= 3 \frac{Nk}{V - Nb} T_i - \frac{N^2}{V^2} a$$

$$= 3 \left[P_i + \frac{N^2}{V^2} a \right] - \frac{N^2}{V^2} a$$

$$= 3P_i + \frac{2N^2}{V^2} a$$

$$P_f > 3P_i$$

Geometrical representation of the states of a gas

So far we describe the states of a gas via:

List possible variables:

$$N, V, P, T$$

↓

Provide pressure equation of state. $P = P(N, V, T)$

Example: Ideal gas

$$PV = NkT$$

$$P = P(N, V, T) = \frac{NkT}{V}$$

Example: v.d. Waals gas

$$\left(P + \frac{N^2}{V^2}a\right)(N - Vb) = NkT$$

$$P = P(N, V, T) = \frac{NkT}{N - Vb} - \frac{N^2}{V^2}a$$

We can represent these geometrically in a space with one dimension for each variable. To simplify this consider the case where N is fixed. Then there are three variables:

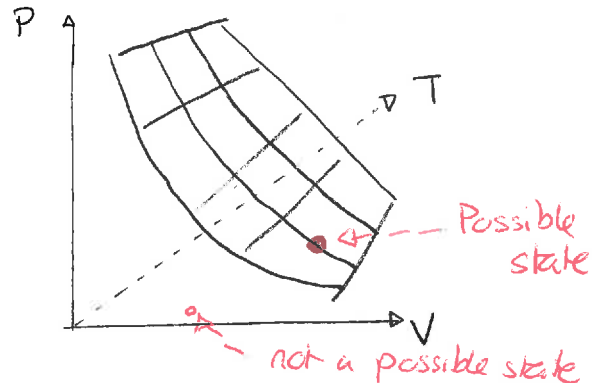
$$P, V, T$$

and one equation relating these.

$$P = P(V, T)$$

This equation describes a two dimensional surface. Then:

Equilibrium states are represented by points on the surface. Points off the surface do not represent states



It follows that non-equilibrium states are not represented by a point on the surface.

The form and shape of the surface depends on the equation of state.. Thus:

Different equations of state generate different surfaces

Demo: Show surface

Finding the equation of state is equivalent to finding the surface. We can therefore use geometrical notions to give an idea for procedures that could give the equation of state.