Fri: HW1 by 5pm

Tues: HW 2 by 5pm

Read 2.22, 2.6

Thermodynamic States: Gas

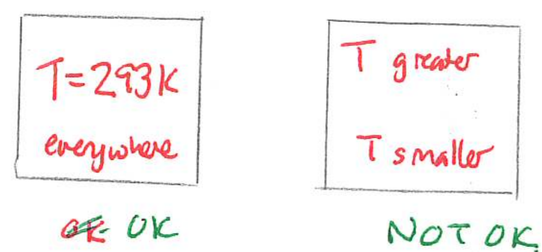
We illustrate the basic ideas and concepts of thermodynamics with a gas.
For the moment, we can describe the state of the gas using bulk variables

N = number of particles

V = volume of gas

P = pressure of gas

T = temperature of gas



We will only consider situations where each variable takes on one value for the entire system. So the pressure is the same throughout the gas. The temperature is also the same throughout the gas. Then we define:

> An <u>equilibrium state</u> of a thermodynamic system is one for which each variable assumes one value for the entire system

We will

1) only consider thermal equilibrium states

2) consider changes from one thermal equilibrium state to another.

Sometimes when a system is in a thermal equilibrium state we say that it is in thermal equilibrium.

DEMO: PSU-5 Free expansion

The free expansion is a process where the pressure of the gas is ill-defined during the process. Initially the system is in an equilibrium state and finally it will reach a new equilibrium but during the process it is not in an equilibrium state.

Thermodynamic States: Nuclear Spins

A nuclear spin is a type of nucleus that has a magnetic dipole moment, which describes how it produces and reacts to magnetic fields. The dipole moment can be thought of as a "bar magnet." Magnetic dipole moments are vectors and they can be measured.

$\nearrow \vec{\mu}$ ← dipole moment

We could consider a large collection of such nuclear spins and describe their equilibrium states as follows:

List bulk variables for the system

N = number of spins

$\vec{M}$ = bulk magnetization $= \sum_{\text{all dipoles}} \vec{\mu}$

T = temperature

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

e.g. $N = 10^{20}$

$\vec{M} = 60\,\text{Am}^2\,\hat{k}$

$T = 500\text{K}$

The subject of thermodynamics:

1) relates the variables for thermal equilibrium and describes how to deduce them from experiment
2) describes process where the system changes from one to another state
3) describes energy and energy flow in terms of the variables
4) describes entropy changes in terms of the variables

Temperature

Temperature appears throughout all thermodynamics and we should try to define it precisely. This should be done so that:

1) the definition does not rely on human sensation
2) the definition does not rely on the particular apparatus or instrument.

The true definition will emerge as a theoretical construct using energy and entropy. But we can provide a more intuitive (but harder to quantify) definition. The basic idea will be:

> Temperature classifies thermodynamic systems according to whether they are in thermal equilibrium with each other.

Thus we must develop a notion of <u>thermal equilibrium between systems.</u> Consider an example:

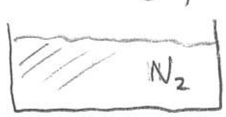
System

Balloon He

at room tem

System

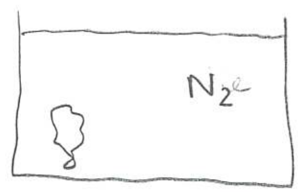
Liquid Nitrogen at boiling point



Initially isolated. Each system is in some thermal equilibrium state

$\rightarrow$

Place balloon in N_2



* the balloon shrinks
  $\Rightarrow$ changes state
* the N_2 evaporates
  $\Rightarrow$ changes state.

The states changed once they were placed in contact. We then say that, prior to contact the systems were <u>not in thermal equilibrium with each other.</u>

Once there are no more changes in the state of each system then we say that they are in thermal equilibrium with each other. In general

> Two systems, A and B, are in thermal equilibrium (with each other) if, once they are placed in thermal contact with each other their states do not change.

Then the basic concept behind temperature is

> Two systems A and B are at the same temperature
> $\Leftrightarrow$ systems A and B are in thermal equilibrium with each other

Do: Example 1a)
Example 1b)
Next page

We would need to check the consistency of this experimental. When this is done we end up with the observation:

> If systems
> * A and B are in thermal equilibrium with each other
> * A and C are in thermal " " " "
>
> then
> * B and C are in thermal equilibrium with each other.

This is the zeroeth law of thermodynamics. This forms the conceptual basis for measuring temperature.

1 Thermal equilibrium and temperature

Consider two balloons, one red and one green, and a bucket of water.

a) Suppose that the red and green balloons have the same temperature. The red balloon is placed into the water and its volume and pressure change noticeably. Was the green balloon in thermal equilibrium with the water (before the red balloon was immersed)? Explain your answer.

b) In a different version of this experiment, the red and green balloons are in thermal equilibrium with each other. The red balloon is also in thermal equilibrium with the water. Is the green balloon in thermal equilibrium with the water? Explain your answer.

Answer: a) The red balloon and water before immersion were not in thermal equilibrium. Thus they had different temperatures; So the green balloon and water also had different temperatures. Thus they were not in thermal equilibrium before immersion.

b) Yes the red and green have the same temperature

red and water " " " "

$\Rightarrow$ green and water have the same temperature

$\Rightarrow$ green and water are in thermal equilibrium

2 Conceptual thermometer

Consider:

- a beaker of water,
- a beaker of ethanol, and
- a resistor, whose resistance can be measured.

The following then occurs:

1. The resistor is immersed in the water and the resistance changes noticeably while there is little observable change in the water.
2. The resistance of the resistor eventually stops changing and reaches a constant value, while immersed in the water.
3. The resistor is removed from the water and immediately immersed in the alcohol. The is no change in the resistance and no observable change in the alcohol.

Are the temperatures of the water and the alcohol the same or different? Explain your answer.

They are the same. After stage 2 the resistor and water are in thermal equilibrium. Stage 3 shows the resistor and alcohol are in thermal equilibrium. Thus the water and alcohol are in thermal equilibrium. Thus they are at the same temperature ∎

So we can use the zeroth law to classify systems into categories so that all systems in one category are in equilibrium with each other. Any system in one category is not in equilibrium with a system in another category. Temperature tracks this:

Two systems have same temp $\Leftrightarrow$ the systems are in thermal equilibrium with each other

Temperatures are then measured using physical devices like the resistor. (or a gas thermometer). These indicate an absolute zero of temperature. The scale that results from this is the Kelvin scale (K).

Equations of state 2.5

We can describe a gas using four variables

N, V, T, P

Observations show that these are not all independent

DEMO: PhET Gas properties

- fix pressure
- add heat - so that ~~the~~ temp doubles

We can see that, if we keep the pressure constant, we can raise the temperature but the volume also changes. There must be a relationship between the bulk variables. In general

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

They will be related by an equation, called the equation of state. The nature of this depends on the gas.

1) Ideal gas

For a dilute gas observations suggest

$$PV = NkT$$ in Kelvin

where $k = 1.38 \times 10^{-23}\ J/K$ is called Boltzmann's constant. This is the ideal gas law and a gas that satisfies this is an ideal gas. When we manipulate the four variables, we decide and can choose which three are independent.

Schematically

List variables for system

N, V, P, T

Provide equation of state

$PV = NkT$

pressure equation of state

Only three variables are independent

One possibility

N, V, T independent

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

Another possibility

N, P, T independent

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

It will be critical, for mathematical correctness, to specify which three are considered independent.

2) <u>van der Waals gas</u>

In real gases:

a) there will be interactions between the gas molecules

b) each molecule occupies a volume in space $\Rightarrow$ V cannot $\to 0$.

A model that accounts for these is the van der Waals model. The equation of state is

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

where a, b are constants that depend on the gas (e.g. O_2 vs N_2). Note

$V - Nb > 0 \quad \Rightarrow \quad V > Nb$ and this reflects the volume occupied by molecules.

3 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.

a) Suppose that the gas is an ideal gas. By what factor does the pressure change?

b) 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) $PV = NkT$

$$P = \frac{NkT}{V} \Rightarrow P = \left(\frac{Nk}{V}\right)T.$$

Then if $T_f = 3T_i$ $\quad P_f = 3P_i$

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

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

Then $$P_i = \frac{k}{V-Nb}T_i - \frac{N^2}{V^2}a$$

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

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

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

$P_f > 3P_i$.

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

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

$V - Nb$

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

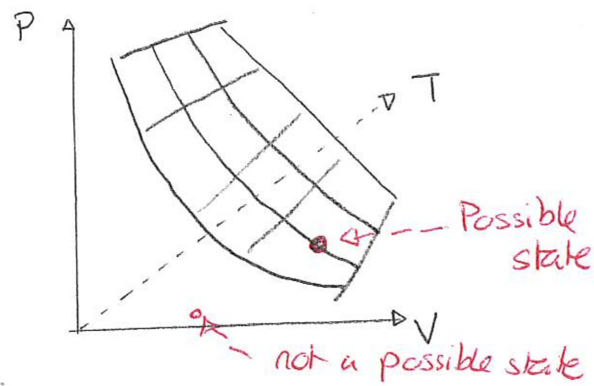
$V - Nb$

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.