Phys 362 2020

Lecture 15

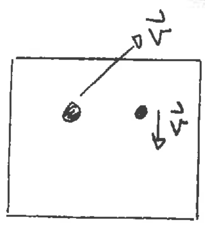
Fri: HW by 5pm

Tues (after break) : Read 4.2

Thermodynamics and microscopic physics

We now aim to connect microscopic physics to thermodynamics. The key idea will be

Particle mass, m.



Describe possible microscopic states of the system

→ Use microscopic states to generate entropy

$$S = S(E,V,N)$$

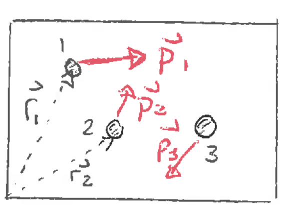
↓ Generate equations of state via:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}$$

→ Produces all thermodynamic relations

Microstates and macrostates: non-interacting gas

We illustrate how some of these ideas unfold for a gas consisting of N non-interacting particles. Then in classical physics the state of these particles is described by listing all positions and velocities (or equivalently momenta)



So a single state of this system is

particle	position	momentum
1	$\vec{r}_1$	$\vec{p}_1$
2	$\vec{r}_2$	$\vec{p}_2$
3	$\vec{r}_3$	$\vec{p}_3$
$\vdots$	$\vdots$	$\vdots$
N	$\vec{r}_N$	$\vec{p}_N$

$\rightsquigarrow$ state

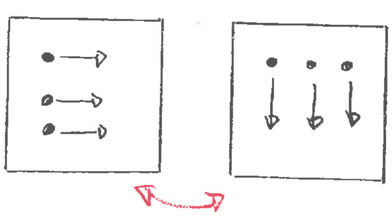
$$s \equiv \{\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2, \dots, \vec{r}_N, \vec{p}_N\}.$$

This type of state is called a microstate since it specifies the microscopic details. For any given microstate we can compute:

1) the number of particles $\equiv N$ (counting)
2) the volume of system $\equiv V$ (by geometry/configuration)
3) the system energy $\equiv E = \sum_{i=1}^{N} \vec{p}_i^{\,2}/2m$ (from microstate)

There are clearly many possible microstates for the system. However many different microstates may share the some bulk properties. The relevant bulk properties will depend on the situation at hand. For example suppose one chooses to describe the bulk system in terms of energy, volume and particle number. Then for any given set of bulk variables there are many possible microstates.

Energy = 100 J

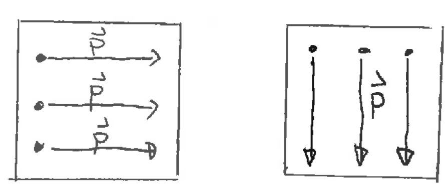


different microstates

Same $\{E,V,N\}$ for every microstate

All represent one macrostate

Energy = 400 J



different macrostates

same $\{E,V,N\}$ for every microstate

differ

All represent another macrostate

Then a <u>macrostate</u> is a state defined by one set of bulk variables. For any single macrostate there are many different possible representative microstates. We will associate an entropy with each macrostate and this entropy $S = S(E, V, N)$ will provide the avenue for generating thermodynamics.

The general scheme will be:

Describe macrostates → Describe constituent /possible microstates for each macrostate

$s_1, s_2, s_3 \ldots$

→ Provide a rule that gives the probabilities with which each microstate occurs

$p(s_1), p(s_2), \ldots$

→ Use probabilities to generate entropy:

S = function of probabilities

This scheme will entail:

1) describing possible constraints on the system and its microstates (e.g. in contact with reservoir at temp T)

2) building a statistical framework for understanding the probabilities in terms of an ensemble of identical physical systems, possibly in different states.

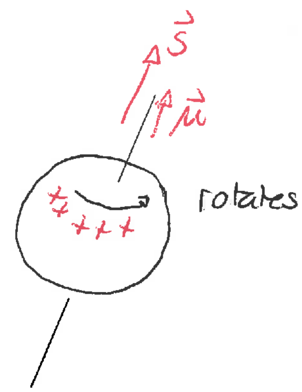
We will illustrate these with:

1) spin-½ systems

2) collections of oscillators (Einstein solid)

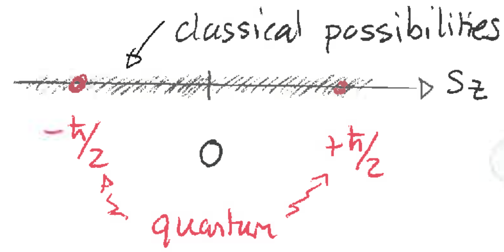
Spin systems

One simple system that illustrates the interplay between thermodynamics and statistical physics is a collection of non-interacting spin-½ particles. A spin-½ particle is a particle with a magnetic dipole moment, $\vec{\mu}$, which is proportional to its spin angular momentum. Such proportionality occurs for rotating charged objects.



In classical physics one can measure every component of the spin simultaneously with arbitrary precision, and the possible outcomes span a continuum. For quantum scale systems (atoms, nuclei, subatomic particles,...) the following occur:

1) For any single component of spin, there are two possible outcomes:



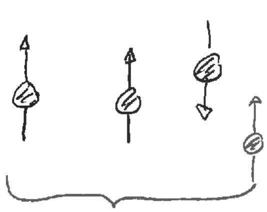
2) There are states that yield either with certainty

spin up $\rightsquigarrow$ $S_z = +\hbar/2$ with certainty	spin down $\rightsquigarrow$ $S_z = -\hbar/2$ with certainty
dipole moment component $\mu_z = +\mu$	dipole moment component $\mu_z = -\mu$

Here μ is the magnitude of the dipole moment

For various reasons we can restrict consideration to the z-direction alone. Each particle is then either in state spin down or spin up. We then define the z-component of magnetization as

$$\boxed{M_z = \sum_{\text{all particles}} \mu_z}$$



$M_z = +2\mu$

When a dipole is placed in an external magnetic field $\vec{B}$ the potential energy is $U = -\vec{\mu}\cdot\vec{B}$. We consider the case where an external field is oriented along $+\hat{z}$. Then for any single dipole the energy is $U = -\mu_z B$. For the entire collection of spin-½ particles is

$$\boxed{E = -BM}$$

We now specify the system in more detail. We assume

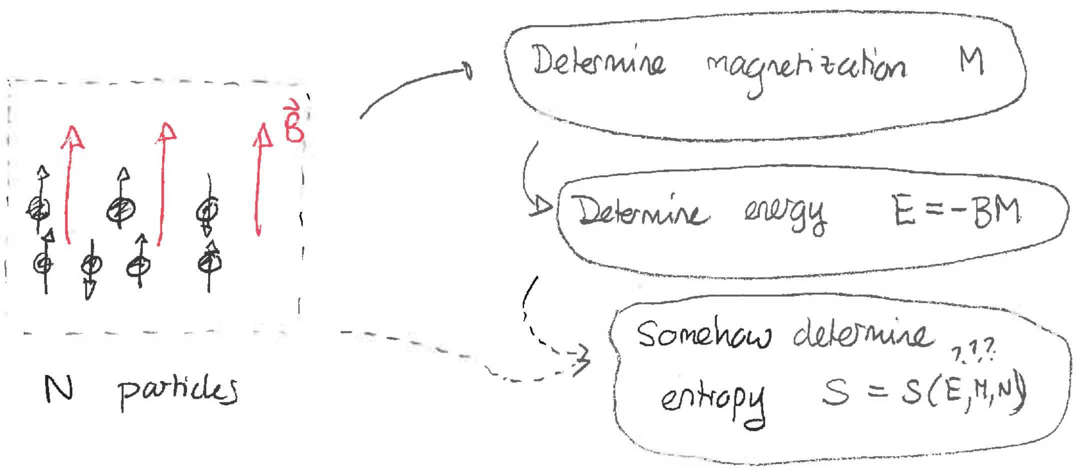
1) there are N spin-½ particles
2) the particles do not interact
3) for any single particle there are two possible states

up : ↑
down : ↓

A macrostate will be specified using.

1) number of particles, N
2) magnetization of ensemble, M
3) energy, $E = -BM$

A microstate will be specified by listing the spin state of each particle:



Microstates and macrostates for spin-1/2 systems

We aim to describe macrostates and associated microstates for spin $\frac{1}{2}$ systems. Consider the magnetization as a macroscopic variable. This can be determined from:

$N_+ =$ number of particles with spin up

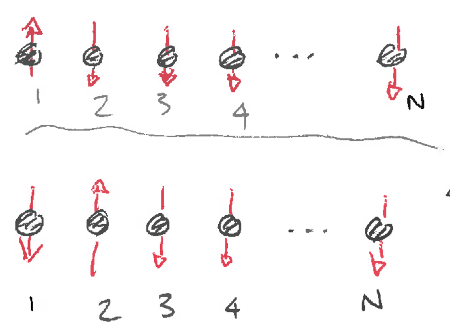
$N_- =$ " " " " " down

Then

$$M = \mu N_+ + (-\mu) N_-$$

$$M = \mu (N_+ - N_-)$$

So we need N_+ and N_- to describe a macrostate:

Macroscopic description	Microscopic description
Provide N_+, N_-	List state of each particle:
one macrostate e.g. $\begin{cases} N_+ = 1 \\ N_- = N-1 \end{cases}$	 different microstates.
Macrostate $\sim$ arrangement of bulk variables	Many macrostates represent one macrostate. **Microstate** $\sim$ arrangement of state of each constituent

We can list and enumerate macrostates and microstates. We need to specify the probability with which each microstate can occur and use these to generate the probabilities for the various macrostates. This depends on the situation:

1) restricted case $(B=0)$

For any single particle:

$$\text{Prob}(\uparrow) = 1/2$$

$$\text{Prob}(\downarrow) = 1/2$$

2) general case $(B \neq 0)$

Here there is a bias toward one state:

$$\text{Prob}(\uparrow) = \frac{1+\epsilon}{2}$$

$$\text{Prob}(\downarrow) = \frac{1-\epsilon}{2}$$

where ϵ depends on B and other parameters, e.g. T, ...

1 Spin system microstates and mascrostates

Consider the case where, for an individual particle, spin up and spin down are equally likely.

a) Show that

$$M = \mu\,(2N_{+} - N)$$

and use this to describe which of N_{+}, N_{-} is/are sufficient to describe any macrostate.

In the following, assume that the system consists of four particles.

b) List all macrostates and, for each, list all possible microstates.

c) What is the probability with which any single microstate occurs?

d) Determine the probability with which each macrostate occurs.

e) Determine the means of N_{+} and M.

Answer: a) $M = \mu(N_{+} - N_{-})$

But $N_{+} + N_{-} = N$

$\Rightarrow \quad N_{-} = N - N_{+}$

$\Rightarrow \quad M = \mu(2N_{+} - N)$

Only need N_{+}

b)

Macrostate	Microstate
$N_{+} = 0$	$\downarrow\downarrow\downarrow\downarrow$
$N_{+} = 1$	$\downarrow\downarrow\downarrow\uparrow$ $\quad \downarrow\downarrow\uparrow\downarrow$ $\quad \downarrow\uparrow\downarrow\downarrow$ $\quad \uparrow\downarrow\downarrow\downarrow$
$N_{+} = 2$	$\uparrow\uparrow\downarrow\downarrow$ $\quad \uparrow\downarrow\uparrow\downarrow$ $\quad \uparrow\downarrow\downarrow\uparrow$ $\quad \downarrow\uparrow\downarrow\uparrow$ $\quad \downarrow\downarrow\uparrow\uparrow$ $\quad \downarrow\uparrow\uparrow\downarrow$
$N_{+} = 3$	$\uparrow\uparrow\uparrow\downarrow$ $\quad \uparrow\uparrow\downarrow\uparrow$ $\quad \uparrow\downarrow\uparrow\uparrow$ $\quad \downarrow\uparrow\uparrow\uparrow$
$N_{+} = 4$	$\uparrow\uparrow\uparrow\uparrow$

c) For each particle either occurs with prob $1/2$

so $\quad \text{prob}(\uparrow\uparrow\uparrow\uparrow) = \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{16}$

Same for all $\Rightarrow \frac{1}{16}$

d) We multiply $\frac{1}{16}$ by number of microstates for each macrostate. This is

$$\binom{N}{N_+} = \frac{N!}{N_+!(N-N_+)!}$$

Macrostate	Prob
$N_+ = 0$	$1/16$
$N_+ = 1$	$4/16$
$N_+ = 2$	$6/16$
$N_+ = 3$	$4/16$
$N_+ = 4$	$1/16$

e) $$\bar{N}_+ = \sum N_+ \, \text{Prob}\,(N_+)$$

$$= 0 \times \frac{1}{16} + 1 \times 4/16 + 2 \times \frac{6}{16} + 3 \times \frac{4}{16} + 4 \times \frac{1}{16}$$

$$= \frac{32}{16} = 2 \quad \Rightarrow \quad \bar{N}_+ = 2$$

$$\bar{M} = \mu(2\bar{N}_+ - N)$$

$$= \mu \, 0$$

$$\Rightarrow \bar{M} = 0$$

This illustrates:

> If there is no external field then all microstates are equally likely.

Then the probability with which any macrostate occurs will be determined partly by the number of microstates that represent that macrostate. We define:

> The <u>multiplicity of a macrostate</u> is:
>
> Ω = number of microstates that represent the macrostate.

Then for an ensemble of N non-interacting spin-½ particles in zero magnetic field

$$\Omega(N_+) = \binom{N}{N_+}$$

This means that, if $B = 0$

$$\text{Prob (macrostate: } N_+) = \frac{\Omega(N_+)}{\text{total number microstates}}.$$

In general:

> Consider a system of N spin-½ particles. Let $p = \text{prob}(\uparrow)$ and $q = \text{prob}(\downarrow)$ then
>
> $$\text{Prob (macrostate } N_+) = \Omega(N_+)\, p^{N_+} q^{N-N_+} = \binom{N}{N_+} p^{N_+} q^{N-N_+}$$