Phys 362 2020

Lecture 19

Fri: HW by 6pm

Tues Read 4.5,

Gas of quantum particles

We aim to build a statistical physics model of non-interacting particles. To do this we considered quantum particles in a cubic well with sides L. The states for a single particle are labeled by three integers n_x, n_y, n_z and the energy of this particle is

$$E = \frac{h^2}{8mL^2}\left[n_x^2 + n_y^2 + n_z^2\right]$$

Now consider N non-interacting distinguishable particles in a box. The state of each needs to be labeled by three integers. Thus we have

#1	#2	#3	...
$n_{1x}\ n_{1y}\ n_{1z}$	$n_{2x}\ n_{2y}\ n_{2z}$	$n_{3x}\ n_{3y}\ n_{3z}$	

and the energy of the collection of these is:

$$E = \frac{h^2}{8mL^2}\left\{n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + n_{2x}^2 + n_{2y}^2 + n_{2z}^2 + \cdots\right\}$$

Again we need to compute

$\Gamma(E)$ = number of states with energy in range $0 \to E$

and the density of states $\qquad g(E) = \frac{d\Gamma}{dE}$

8 Density of states: multiple distinguishable quantum particles in a box

Consider a cubic box with sides of length L.

a) Suppose that there are three particles. List the states corresponding to the two lowest energies.

b) Now suppose that there are N particles. Give the condition that the integers $n_{1x}, n_{1y}, \ldots$ must satisfy in order to determine $\Gamma(E)$. Express this in terms of a volume.

One can show that the volume of an n dimensional hypersphere of radius R is

$$V = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n$$

where $\Gamma(m)$ is the gamma function. This has properties

$$\Gamma(m+1) = m\Gamma(m)$$
$$\Gamma(1/2) = \sqrt{\pi}$$
$$\Gamma(1) = 1.$$

c) Determine the density of states and entropy for this system

d) Determine the energy equation of state. Do you recognize it?

e) Determine the pressure equation of state. Do you recognize it?

Answer a) $E = \frac{h^2}{8ML^2}\left[n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + n_{2x}^2 + n_{2y}^2 + n_{2z}^2 + n_{3x}^2 + n_{3y}^2 + n_{3z}^2 \right]$

n_{1x}	n_{1y}	n_{1z}	n_{2x}	n_{2y}	n_{2z}	n_{3x}	n_{3y}	n_{3z}	$E/\frac{h^2}{8ML^2}$
1	1	1	1	1	1	1	1	1	9
1	1	2	1	1	1	1	1	1	12
1	2	1	1	1	1	1	1	1	12
2	1	1	1	1	1	1	1	1	12
1	1	1	1	1	2	1	1	1	12
1	1	1	1	2	1	1	1	1	12
1	1	1	2	1	1	1	1	1	12
1	1	1	1	1	1	1	1	2	12
1	1	1	1	1	1	1	2	1	12
1	1	1	1	1	1	2	1	1	12

b) We need

$$0 \le \left(n_{1x}^2 + n_{2y}^2 + n_{1z}^2 + \cdots + n_{Nx}^2 + n_{Ny}^2 + n_{Nz}^2 \right) \le \frac{8mL^2}{h^2} E$$

There are 3N parameters. The previous geometrical argument implies that these occupy a sector of a 3N dimensional sphere with radius $8mL^2 E/h^2$. The particular sector is $1/2^{3N}$ of the volume of the entire sphere. Then

$$\Gamma(E) = \frac{1}{2^{3N}} \times \text{volume of 3N dim hypersphere radius} \sqrt{\frac{8mL^2}{h^2}E}$$

c) $$\text{Volume} = \frac{2\pi^{3N/2}}{3N\,\Gamma(3N/2)} \left(\frac{8mL^2}{h^2}\right)^{\frac{3N}{2}} E^{3N/2}$$

$$\Rightarrow \Gamma(E) = \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{3N\,\Gamma(3N/2)} \left(\frac{8mL^2}{h^2}\right)^{\frac{3N}{2}} E^{3N/2}$$

$$= \frac{2}{3N\,\Gamma(3N/2)} \left(\frac{\pi\, 8m}{4h^2}\right)^{3N/2} L^{3N} E^{3N/2}$$

$$\Rightarrow \Gamma(E) = \frac{1}{\frac{3N}{2}\Gamma\left(\frac{3N}{2}\right)} \left(\frac{2\pi m}{h^2}\right)^{3N/2} V^N E^{3N/2}$$

$$\Gamma(E) = \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)} \left(\frac{2\pi m}{h^2}\right)^{3N/2} V^N E^{3N/2}$$

Then

$$g(E) = \frac{d\Gamma}{dE} = \frac{\cancel{3N/2}}{\cancel{\frac{3N}{2}}\,\Gamma\left(\frac{3N}{2}\right)} \left(\frac{2\pi m}{h^2}\right)^{3N/2} V^N E^{3N/2-1}$$

The entropy is

$$S(E,V,N) = k \ln\left[g(E)\,dE\right]$$

$$= k \ln\left[\frac{1}{\Gamma\left(\frac{3N}{2}\right)}\left(\frac{2\pi m}{h^2}\right)^{3N/2} V^N E^{3N/2-1}\, dE\right]$$

$$= k N \ln(V) + k\left(\frac{3N}{2}-1\right)\ln(E) + k \ln\big[\underbrace{f(N)}_{\frac{1}{\Gamma\left(\frac{3N}{2}\right)}\left(\frac{2\pi m}{h^2}\right)^{3N/2}}\big] + k\ln(dE)$$

If $N \gg 1$ then

$$S(E,V,N) = kN \ln V + k\frac{3N}{2}\ln(E) + \cdots$$

d) $\frac{1}{T} = \frac{\partial S}{\partial E} = k\frac{3N}{2}\frac{1}{E} \Rightarrow E = \frac{3}{2}NkT$

e) $\frac{P}{T} = \frac{\partial S}{\partial V} \Rightarrow \frac{P}{T} = kN/V \Rightarrow PV = NkT$ $\blacksquare$

Thus we get:

For a gas of distinguishable quantum particles in a box $\Gamma(E,V,N) = \frac{1}{\Gamma\left(\frac{3N}{2}+1\right)}\left[\frac{2\pi m}{h^2}\right]^{3N/2} V^N E^{3N/2}$

Then the identification

$$\Omega(E) = \frac{d\Gamma}{dE}\,dE \qquad \text{plus} \qquad S(E,V,N) = k\ln\left[\Omega(E,V,N)\right]$$

results in the equations of state for a monoatomic ideal gas

Two issues with this are:

1) the approach involves a hybrid of quantum physics and classical physics. Surely there is a purely classical approach that gives the equation of state of an ideal gas.

2) the approach assumes that the particles are distinguishable. If the particles were indistinguishable the number of states $\Gamma(E)$ would be different. This is important because the chemical potential is derived from

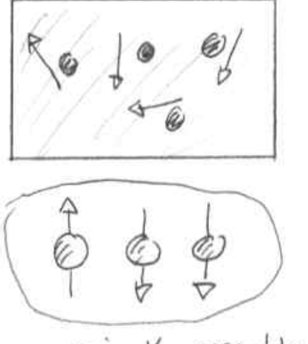
$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

and $S = k\ln\left[g(E,V,N)\,dE\right]$ would depend on the counting of the states. We need to correct this later.

Ensembles of systems

We will often consider a system which consists of a collection of identical particles. The issue then is how to describe the entire system in terms of the states for an individual particle in the system. Recall the scheme

classical gas



spin-½ ensemble

Macrostates described via:
total energy E
particle number N
(other variables: V)

$\rightarrow$

Determine multiplicity for each macrostate. Thus count microstates for the entire system:
$\Omega(E,N)$ = # microstates with energy E

$\rightarrow$

Entropy
$$S = k\ln\left[\Omega(E,N)\right]$$

We will now reformulate this in such a way that it generalizes to describe systems beyond those with one fixed energy and so that calculations of entropy and other thermodynamic quantities are facilitated. The scheme is:

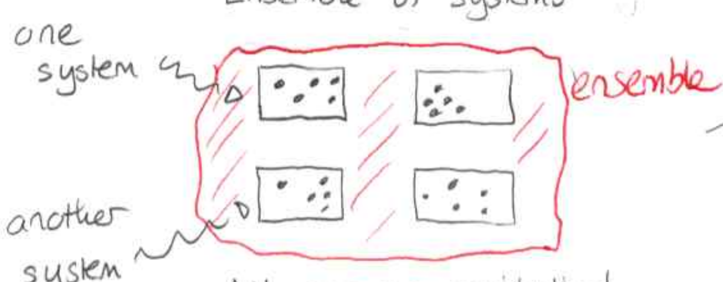
Describe system and its possible states: $\{s\}$

→ Obtain rules for the probability with which the system could be in state "s": prob $= p_s$

→ Use probabilities to determine entropy

We will apply this to an ensemble of systems, called the microcanonical ensemble and show that it generates entropy $S = k \ln[\Omega]$ as we had before. We can subsequently apply it to other ensembles. First we consider an ensemble of systems. This is a conceptual idea that enables us to understand the subsequent probability description.

Ensemble of systems



All systems are identical but they could be in different states

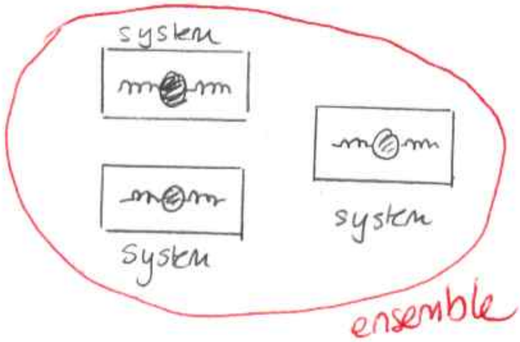
→ List possible states for a single ensemble member

→ Determine probability with which each state occurs

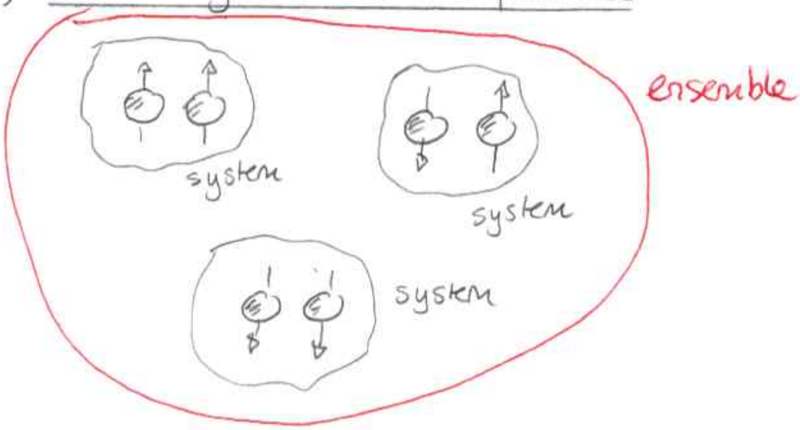
→ Calculate entropies from probabilities

The resulting formalism will encompass ensembles whose members have few constituents as well as those with many constituents.

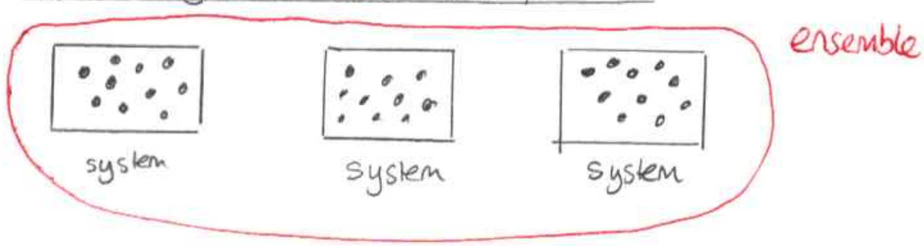
1) <u>each system has one particle</u>



2) <u>each system has two particles</u>



3) <u>each system has many particles</u>



Once we have settled on the meaning of the "system" we then need to describe

1) possible states of the system
2) energy of each state.

Some examples are:

1) one dimensional harmonic oscillator.

- quantum physics labels states as $n = 0, 1, 2, \ldots$
- use $s = n$ (one natural number)

2) particle in a one dimensional well

- quantum physics labels states as $n = 1, 2, 3$
- use $s = n$ (one integer)

3) single hydrogen atom:

- quantum physics labels states using (n, ℓ, m_ℓ, m_s)

$n = 1, 2, 3$

$\ell = 0, 1, 2, \ldots, n-1$

$m_\ell = -\ell, -\ell+1, \ldots \ell-1, \ell$

$m_s = +\frac{1}{2}, -\frac{1}{2}$

- use $s \equiv (n, \ell, m_\ell, m_s)$ (collection of four numbers)

2 System states

For each of the following systems list the possible states in order of increasing energy and provide the energies

a) A pair of non-interacting, distinguishable identical one dimensional quantum oscillators.

b) A single particle in a two dimensional infinite square well with sides of length L.

Answer: a) For each oscillator the states are labeled

$n = 0, 1, 2, \ldots$

and the energy is $E_n = \hbar\omega(n + 1/2)$

Call one oscillator "A" and the other "B". Then

n_A	n_B	E (both)	State label
0	0	$\hbar\omega$	s=1
0	1	$2\hbar\omega$	s=2
1	0	$2\hbar\omega$	s=3
1	1	$3\hbar\omega$	s=4
0	2	$3\hbar\omega$	s=5
2	0	$3\hbar\omega$	s=6

b) The states are labeled n_x, n_y and $E = \frac{h^2}{8mL^2}(n_x^2 + n_y^2)$

n_x	n_y	E	State label
1	1	$2\ h^2/8mL^2$	s=1
1	2	$5\ h^2/8mL^2$	s=2
2	1	$5\ h^2/8mL^2$	s=3
2	2	$8\ h^2/8mL^2$	s=4

Thus we can describe the states of the ensemble members via a collection of labels $\{s\}$. For each possible state:

$$\boxed{p_s := \text{probability with which ensemble member is in state } s}$$

We can then show that, for an ensemble of such systems

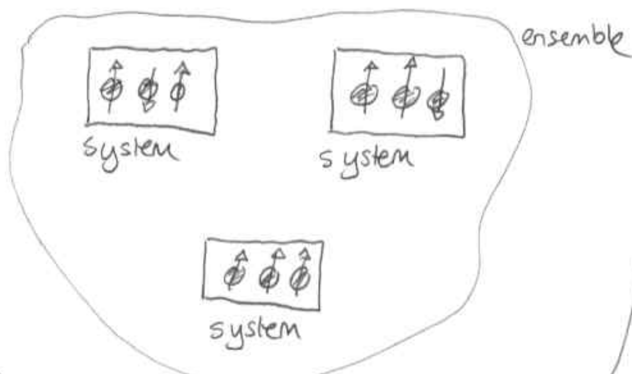
The average entropy per system in the ensemble is:

$$S = -k \sum_{\text{all states "s"}} p_s \ln[p_s]$$

where p_s is the probability with which the system is in state s.

To do this construction: consider

A single "supersystem" consisting of ν ensemble members (systems)



$\longrightarrow$ Determine multiplicity of supersystem in terms of individual systems Ω

$\downarrow$

$S = k \ln \Omega$

Proof: Suppose that

$$\left.\begin{aligned} \nu &= \text{total number of systems} \\ \nu_1 &= \text{number in state } s=1 \\ \nu_2 &= \quad " \quad " \quad " \quad s=2 \\ &\vdots \end{aligned}\right\} \quad \nu = \sum_{\text{all } s} \nu_s$$

Now the multiplicity for this "superstate" for the "supersystem", Ω can be determined by counting the number of ways to arrange ν systems into $\nu_1, \nu_2, \ldots$ This is

$$\Omega = \frac{\nu!}{\nu_1!\,\nu_2!\,\nu_3!\ldots}$$

So

$$\begin{aligned} S &= k \ln \Omega \\ &= k\left\{\ln \nu! - \sum_s \ln \nu_s!\right\} \end{aligned}$$

Using Stirling's approximation

$$\ln(\nu!) \approx \nu \ln \nu - \nu$$

$$\ln(\nu_s!) \approx \nu_s \ln \nu_s - \nu$$

$$\begin{aligned} \Rightarrow \quad S &\approx k\left\{\nu \ln \nu - \nu - \sum_s (\nu_s \ln \nu_s - \nu_s)\right\} \\ &= k\left\{\nu \ln \nu - \nu - \sum_s \nu_s \ln \nu_s + \underbrace{\sum \nu_s}_{\nu}\right\} \\ &= k\left\{\nu \ln \nu - \sum_s \nu_s \ln \nu_s\right\} \end{aligned}$$

Then the probability of finding a system in state s is

$$p_s = \nu_s / \nu \qquad \Rightarrow \qquad \nu_s = \nu p_s$$

So

$$\sum_s \nu_s \ln \nu_s = \sum_s \nu p_s \ln(\nu p_s)$$

$$= \nu \sum_s p_s (\ln \nu + \ln p_s)$$

$$= \nu \ln \nu \underbrace{\sum_s p_s}_{=1} + \nu \sum_s p_s \ln p_s$$

So

$$S = k\left\{\cancel{\nu \ln \nu} - \cancel{\nu \ln \nu} - \nu \sum_s p_s \ln[p_s]\right\}$$

$$= -k\nu \sum_s p_s \ln p_s$$

The average entropy per ensemble member is S/ν which is

$$-k \sum_s p_s \ln(p_s) \qquad \blacksquare$$