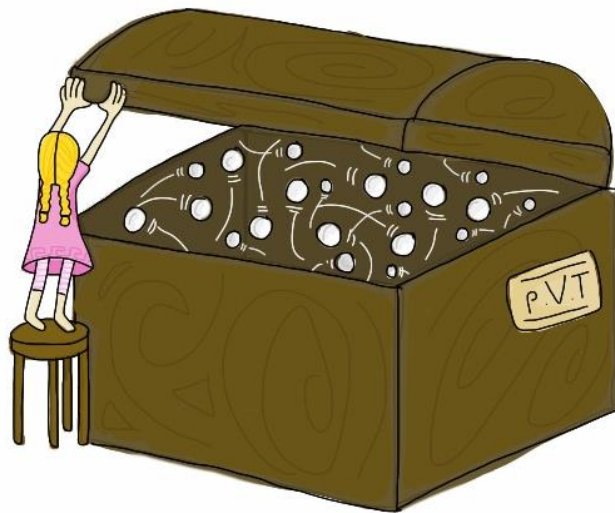


## PH20029 Thermal Physics

Statistical Mechanics notes, Dr Anton Souslov

These notes only cover statistical mechanics. Classical thermodynamics is taught by Dr Zeidler. The notes are based on lectures of Prof Tim Birks and Dr Enrico Da Como of the past few years.

**Statistical mechanics** is the study of thermodynamic systems (such as an ideal gas) based on the postulate that these systems are composed of atomic-scale constituents, the motion of which is not known. The results of classical thermodynamics arise from averages of their properties.



**Revision:** You will need material from previous units, including:

- discrete statistics: factorials, the  ${}^nC_r$  formula, averages
- anything you may know about continuous distributions and probability density functions will be very useful
- series: Taylor series, binomial theorem, geometric progressions
- functions: hyperbolic functions ( $\sinh$ ,  $\cosh$ ,  $\tanh$ ) are useful
- Properties of Matter
- and (of course) the thermodynamics in the first part of the unit

These notes cover the following topics (and there are appendices at the end):

1. (p. 4) ***Introduction***

Three types of states, the postulates of statistical mechanics, the thermodynamic limit.

2. (p. 11) ***The closed system***

Boltzmann's entropy, deriving the laws of thermodynamics, the statistical weight function, two-level systems.

3. (p. 24) ***System at constant temperature***

The Boltzmann distribution, the partition function, levels and states, continuous distributions, many particle systems, the ideal classical gas, distinguishability.

4. (p. 44) ***System at constant  $T$  and  $\mu$***

The Gibbs distribution, the grand partition function, the ideal quantum gas, the Fermi-Dirac and Bose-Einstein distributions, fermion and boson gases, Planck's radiation law.

Headers summarise what's on each page, and also indicate a typical (no promises!) lecture number when it's covered.

If you decide to print these notes I recommend double-sided black and white, "2 on 1" page layout and "short edge" binding location. At 2013 prices this costs about 90p using University printers. The notes are designed to be comfortable to read at this size, without needing colour.

***The Moodle page*** for the unit contains:

*Forum:* For you to post questions about unit material (much better than email), and to read important announcements

*Organisational information* (when different lectures and problems classes will be held, etc). I will assume you have read this and will keep checking for changes from time to time, especially if you miss any announcements in lectures.

*Problem sheets* as pdf files. I will not be handing out paper copies. You can print them yourself or ask me. Please attempt the questions well before the associated problems classes.

*Model answers* to problem sheets. These will become available after the corresponding problems classes. The idea is to attempt the problems before being given the answers!

***Health warning :***

Our statistical mechanics is based on a quantum mechanical description of particles. If your course does not include quantum mechanics, it may help you to do some of your own studies of the subject, in order to follow the statistical mechanics.

However, the key results are given to you in these notes.

FYI the symbol  $\hbar$  "h-bar" is widely used in quantum mechanics and represents Planck's constant  $h$  divided by  $2\pi$ .

***To contact me*** outside timetabled contact time, use the Moodle forum or email (A.Souslov@bath.ac.uk)

## 1. Introduction: statistical mechanics

... is thermodynamics based on the statistics of microscopic (ie, atomic-level) degrees of freedom.

We consider *three types of states* - different ways of describing a complex system with many parts.

**Macrostates** are a coarse description of the system, specified by a few "macro" observables only. These are the states considered in classical thermodynamics, the first half of the unit.

eg,  $p$ ,  $V$  and  $T$  (or  $U$ ,  $V$  and  $N$ ) for an ideal gas in eq<sup>m</sup> 

**Microstates** are a complete description of the system on the atomic scale.

eg, the positions and velocities of all the molecules in a gas

A microstate that is consistent with a given macrostate (eg, with the right total  $U$ ,  $V$  and  $N$ ) is called *accessible* or *available*.

For each macrostate there are typically  $\gg 10^{N_A}$  accessible microstates! The microstate usually cannot be known in practice  $\Rightarrow$  analyse statistically.

**Single-particle states (SPS's)** are the states of one particle ignoring the others.

eg, the position and velocity of one molecule in a gas

The microstates of a system of *weakly-interacting particles* can be built up from the SPS's of each particle.

## Distinguishability

The particles in a system are *distinguishable* if there is some way to identify individual particles and tell them apart from the others. You can imagine that they carry labels or ID numbers, or perhaps different colours, or fixed locations that act as addresses. They may also have different physical properties, but usually we assume that (apart from the distinguishing "labels") they are identical.

In contrast, we can't tell *indistinguishable* particles apart even in principle. A microstate may therefore be unchanged if two indistinguishable particles are exchanged. In due course we will see that most types of matter is composed of indistinguishable particles and that this fact has profound physical consequences.

## Postulates of statistical mechanics

1. microstates exist
  2. energy is conserved
  3. the principle of equal a priori probabilities:  
a *closed* system in  $eq^m$ , in a given macrostate, is equally likely to be in any of its accessible microstates
- NB!
- 
- The diagram consists of a large red bracket on the right side of the first two postulates, with the text "(yawn...)" to its right. Two red arrows originate from the "NB!" text: one points to the first postulate "microstates exist" and the other points to the second postulate "energy is conserved".

... because, if all we know is the macrostate, we have no reason to favour one unobservable microstate over another (we're ignorant) and the microstate is always changing anyway, eg as molecules collide (we can't keep up).

Statistical weight of a macrostate

Different macrostates are *not* equally likely; they may have different numbers of (equally likely) accessible microstates. The probability of a given macrostate  $i$  is proportional to its number of accessible microstates, known as its *statistical weight*  $W_i$ :

statistical weight  $W_i$  = number of accessible microstates

$$\begin{aligned} \text{probability } P_i &\propto W_i \\ &= \frac{W_i}{\text{total number of microstates}} \end{aligned}$$

Example (a deck of cards)

The *statistical weight* of a club card in a regular deck of cards is  $W_{club} = 13$ , since there are 13 clubs in a deck. For a system comprising a card drawn at random from the deck, "club card" is an example of a macrostate and "ace of clubs" is an example of one of the microstates that are accessible to that macrostate.

The statistical weight of a queen is  $W_{queen} = 4$ , since there are 4 queens in a deck. A randomly-drawn card is  $W_{club}/W_{queen} = 13/4$  times more likely to be a club than a queen. This is just the *definition* of a statistical weight.

The *probability* of drawing a club card is

$$P_{club} = \frac{W_{club}}{\text{no. cards}} = \frac{13}{52} = \frac{1}{4}$$

since there are 52 cards altogether in a deck.

### Example (tossing coins)

$N = 10$  distinguishable coins are thrown randomly onto a table.

*Macrostate*: the number  $n$  of "tails" T ( $\Rightarrow N - n$  "heads" H)

one variable with 11 possible values (eg,  $n = 6$ )

*Microstate*: the complete *ordered* list of T's and H's

10 variables with 2 possible values each (eg, "THHTTTHHTT")

*SPS*: one coin is either T or H

1 variable with 2 possible values (eg, "T")

Each (ordered) microstate is equally likely, eg "TTTTTTTTTT" is just as likely as "THTHHHTTHT". But there are many more cases with  $n = 5$  (all looking superficially similar) than with  $n = 10$ , so the macrostates are *not* equally likely:

[illegible]

The statistical weight  $W(n)$  of the macrostate with  $n$  tails  
= number of ways to divide  $N$  coins between 2 sets (tails and heads) with  $n$  coins in the first set and  $N - n$  in the second set.

This is a binomial distribution (see Appendix A.4):

$$W(n) = {}^N C_n = \frac{N!}{n!(N-n)!}$$

eg for  $N = 10$ :

$$W(5) = \frac{10!}{5! \times 5!} = 252$$

$$W(10) = \frac{10!}{10! \times 0!} = 1$$

The  $n = 5$  macrostate is  $252 \times$  more likely than the  $n = 10$  macrostate, even though all the microstates are equally likely.

The *probability* of the macrostate  $n$  is

$$P(n) = \frac{W(n)}{2^N} \quad [2^N \text{ cases in total}]$$

eg for  $N = 10$ :

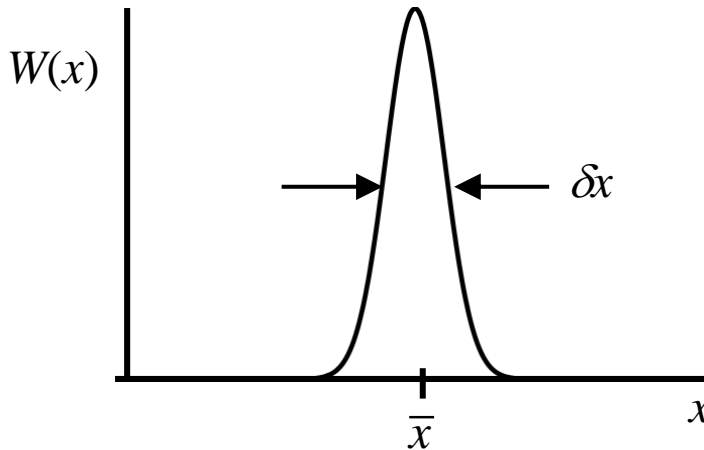
$$P(5) = \frac{W(5)}{2^{10}} = \frac{252}{1024} \approx 25\%$$

$$P(10) = \frac{W(10)}{2^{10}} = \frac{1}{1024} \approx 0.1\%$$



The "thermodynamic limit" (large  $N$ )

Statistical weight functions  $W(x)$  usually peak near the mean value of the macrostate variable  $x$ .



For large numbers of particles  $N$ , the peak becomes very narrow ( $\delta x \propto 1/\sqrt{N}$ ) and the mean value of  $x$  becomes the overwhelmingly likely value of  $x$ . The probability that the observed macrostate differs significantly from the most probable macrostate becomes negligible.

Therefore, in the so-called *thermodynamic limit*  $N \rightarrow \infty$ ,

the system will appear to choose the macrostate with the greatest statistical weight (ie, with the most accessible microstates).

so the mean macrostate variable  $x$  of the system is found by solving

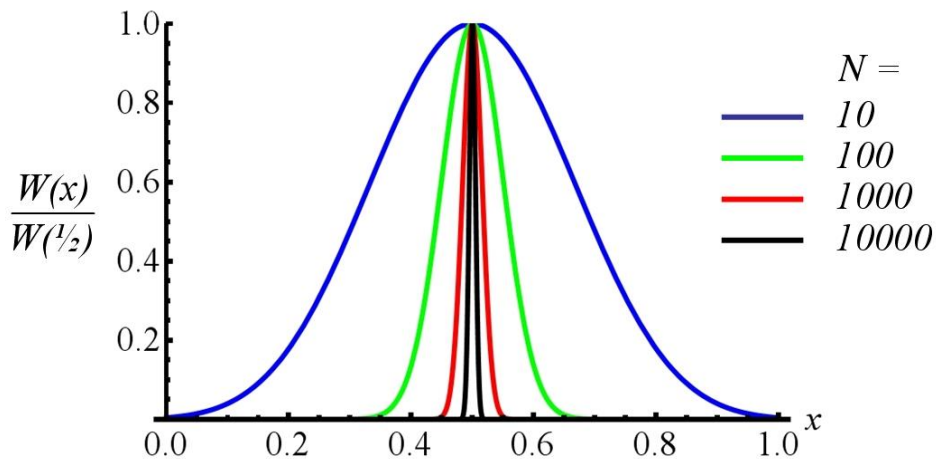
$$\frac{\partial W}{\partial x} = 0 \quad \text{[calculus max/min]}$$

Example (tossing coins)

Consider the system of  $N$  coins:

$$W(n) = \frac{N!}{n!(N-n)!}$$

To compare this distribution for different values of  $N$ , express it in terms of the fraction  $x = n/N$  of coins that are tails, which always lies between 0 and 1. Also, because  $W$  becomes very large, (eg the peak value of  $W$  for  $N = 10\,000$  is  $\sim 10^{3000}$ ), plot  $W(x)$  divided by its peak value:



All the distributions are peaked at  $x = 1/2$ , but the width of the peak gets narrower as  $N$  increases. For values of  $N$  of the order of Avogadro's number  $N_A$ , which are typical in statistical mechanics, the width of the peak is truly insignificant.

For large  $N$ , the observed value of  $x$  will be negligibly different from  $1/2$ , the value at the peak of  $W(x)$ .

In these lectures we will look at three generic thermodynamic systems, with different physical quantities held constant.

## 2. The closed system

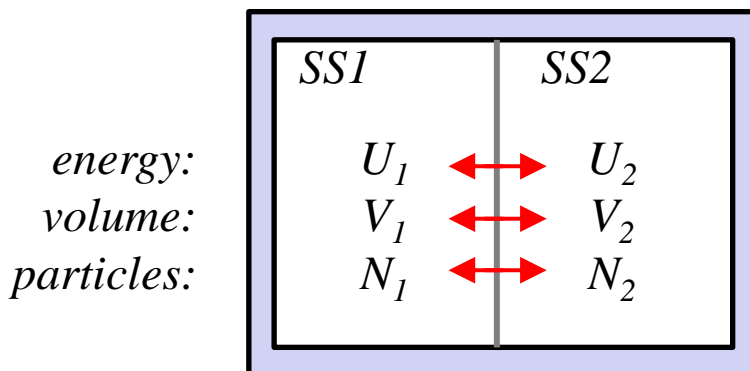
(a.k.a. *micro-canonical ensemble*)

By studying this system we will *derive* the laws of thermodynamics!

A closed system is completely isolated: it does not exchange energy, volume or particles with its surroundings.


$$\text{constant} \left\{ \begin{array}{l} \text{internal energy } U \\ \text{volume } V \\ \text{no. particles } N \end{array} \right.$$

Divide it into sub-systems SS1 and SS2 with a wall that can transfer energy (as heat), volume (by moving) and particles (permeable) between the sub-systems.



$$\text{total} \left\{ \begin{array}{l} U_0 = U_1 + U_2 \\ V_0 = V_1 + V_2 \\ N_0 = N_1 + N_2 \end{array} \right\} \text{fixed}$$

Entropy

The macrostate of SS1 is determined by its macro variables  $U_1$ ,  $V_1$  and  $N_1$ . Hidden beneath this simple description is a vast number of accessible (but unobservable) microstates, all with matching values for these three "summary" variables. SS1 could be in any of these microstates. Counting them gives the statistical weight  $W_1(U_1, V_1, N_1)$  of the macrostate. 

Likewise the statistical weight of the corresponding macrostate of SS2, with macro variables  $U_2$ ,  $V_2$  and  $N_2$ , is  $W_2(U_2, V_2, N_2)$ .

The macrostate of the whole system is determined jointly by the macrostates of SS1 and SS2. Since the microstate of SS1 is independent of the microstate of SS2, the statistical weight of the whole system is

$$W = W_1 \times W_2 \quad [\text{Appendix A.2}]$$

$$\Rightarrow \ln(W) = \ln(W_1) + \ln(W_2) \quad \leftarrow \text{Red arrow pointing from the text below}$$

Note that  $\ln(W)$  behaves just like entropy:


- it is an extensive (additive) variable
- it is maximised in closed systems in eq<sup>m</sup>

[thermodynamic limit - page 9]

Boltzmann *defined* entropy in statistical mechanics to be

$$S = k_B \ln W$$

with Boltzmann's constant  $k_B$  introduced to match units and values with the "old" entropy of thermodynamics.

*this is where we use the principle of a priori probabilities* 

The conditions for eq<sup>m</sup>

At eq<sup>m</sup>,  $\ln(W)$  is a maximum (thermodynamic limit). We maximise  $\ln(W)$  with respect to three variables  $U_2$ ,  $V_2$  and  $N_2$ , because  $U_1$ ,  $V_1$  and  $N_1$  are not independent of them. (For example  $U_1$  is given by  $U_0 - U_2$  where  $U_0$  is the *constant* total internal energy of the whole system.)

1. With respect to energy  $U_2$  (thermal eq<sup>m</sup>)

$$\left( \frac{\partial \ln W}{\partial U_2} \right)_{V_2, N_2} = 0 \quad [\text{calculus max/min}]$$

$$\frac{\partial \ln W_2}{\partial U_2} + \frac{\partial \ln W_1}{\partial U_2} = 0 \quad [\ln W = \ln W_1 + \ln W_2]$$

$$\frac{\partial \ln W_2}{\partial U_2} = - \frac{\partial \ln W_1}{\partial U_1} \times \frac{dU_1}{dU_2} \quad [\text{chain rule}]$$

$$= \frac{\partial \ln W_1}{\partial U_1} \quad [U_1 = U_0 - U_2 \Rightarrow dU_1/dU_2 = -1]$$

Therefore there is a quantity  $\beta = \partial \ln W / \partial U$  which must be equal for two systems to be in thermal eq<sup>m</sup>, so that heat doesn't flow between them. The existence of such a quantity

$\Rightarrow$  **the zeroth law of thermodynamics**

with  $\beta$  determining the *temperature*  $T$ . To match units:

$$\boxed{\beta = \frac{1}{k_B T} = \left( \frac{\partial \ln W}{\partial U} \right)_{V, N}} \quad \text{or} \quad \boxed{T = \left( \frac{\partial U}{\partial S} \right)_{V, N}}$$

2. With respect to volume  $V_2$  (mechanical eq<sup>m</sup>)

$$\left( \frac{\partial \ln W}{\partial V_2} \right)_{U_2, N_2} = 0 \quad [\text{calculus max/min}]$$

$$\Rightarrow \frac{\partial \ln W_2}{\partial V_2} = \frac{\partial \ln W_1}{\partial V_1} \quad [\text{same reasoning as before}]$$

Therefore  $\partial \ln W / \partial V$  must be equal for mechanical eq<sup>m</sup>, so the subsystems don't exchange volume by movement of the wall. It therefore determines the *pressure*  $p$ . To match units:

$$p = k_B T \left( \frac{\partial \ln W}{\partial V} \right)_{U, N} = T \left( \frac{\partial S}{\partial V} \right)_{U, N}$$

3. With respect to no. particles  $N_2$  (diffusive eq<sup>m</sup>)

$$\left( \frac{\partial \ln W}{\partial N_2} \right)_{U_2, V_2} = 0 \quad [\text{calculus max/min}]$$

$$\Rightarrow \frac{\partial \ln W_2}{\partial N_2} = \frac{\partial \ln W_1}{\partial N_1} \quad [\text{same reasoning as before}]$$

Therefore  $\partial \ln W / \partial N$  must be equal for diffusive eq<sup>m</sup>, so the subsystems don't exchange particles. It therefore determines the *chemical potential*  $\mu$ , an intensive variable related to  $N$  like  $p$  relates to  $V$ . To match units:

$$\mu = -k_B T \left( \frac{\partial \ln W}{\partial N} \right)_{U, V} = -T \left( \frac{\partial S}{\partial N} \right)_{U, V}$$

The thermodynamic identity

Since entropy  $S$  is a function of  $U$ ,  $V$  and  $N$ :

$$\begin{aligned}dS &= \frac{\partial S}{\partial U} dU + \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial N} dN && \text{[chain rule for partials]} \\&= k_B \frac{\partial \ln W}{\partial U} dU + k_B \frac{\partial \ln W}{\partial V} dV + k_B \frac{\partial \ln W}{\partial N} dN && [S = k_B \ln W] \\&= \frac{dU}{T} + \frac{pdV}{T} - \frac{\mu}{T} dN && \text{[found in last 2 pages]}\end{aligned}$$

Rearrange for  $dU$ :

$$\boxed{dU = TdS - pdV + \mu dN}$$

the thermodynamic identity (generalised to variable  $N$ )

$\Rightarrow$  **the first law of thermodynamics.**

(Although the most important consequence of the first law - that energy is conserved - was in fact one of our three postulates...)

Approaching thermal eq<sup>m</sup>

The two subsystems exchange some energy (with  $V$  and  $N$  fixed) as they approach eq<sup>m</sup>. The total entropy  $S_0$  increases:

$$\delta S_0 = \delta S_1 + \delta S_2 \geq 0 \quad [\text{total entropy } S_0 \text{ increases}]$$

$$\frac{\partial S_1}{\partial U_1} \delta U_1 + \frac{\partial S_2}{\partial U_2} \delta U_2 \geq 0 \quad [\text{chain rule, fixed } V \text{ and } N]$$

$$\left( \frac{\partial S_2}{\partial U_2} - \frac{\partial S_1}{\partial U_1} \right) \delta U_2 \geq 0 \quad [\text{constant total } U \Rightarrow \delta U_1 = -\delta U_2]$$

$$\left( \frac{1}{T_2} - \frac{1}{T_1} \right) \delta U_2 \geq 0 \quad \left[ \frac{1}{T} = \frac{\partial S}{\partial U} \right]$$

ie, SS2 gains energy ( $\delta U_2 > 0$ ) if and only if  $T_2 < T_1 \Rightarrow$  heat always flows from the hotter sub-system to the colder one  
 $\Rightarrow$  **the second law of thermodynamics.**

Conclusions

1. If you can find an expression for the number of accessible microstates  $W$  of a closed system (ie, a single function), you can deduce  $S$ ,  $T$ ,  $p$ ,  $\mu$  and hence other thermodynamic functions.
2. The statistics of coin tossing  $\Rightarrow$  the laws of thermodynamics!
3. Thermodynamics is statistical: in a given experiment there is in theory a (very very small) chance that heat will flow from a colder subsystem to a hotter one.



"Two level" systems (just two SPS's)

Example: spin system

Q. Each of  $N$  atoms ( $N$  large) in a magnetic field can be in one of two SPS's:

"spin up" with energy  $E_0$ , or

"spin down" with energy  $-E_0$ . \*

Find the temperature  $T$  as a function of internal energy  $U$ .

(Assume the atoms are distinguishable, eg they are fixed and so can be identified by their locations.)

A. To find  $T$  we need to find  $W(U)$  and then use

$$\frac{1}{k_B T} = \frac{\partial \ln W}{\partial U}$$

We can find  $W(n)$  from binomial statistics: the number of microstates with a total of  $n$  "spin up" atoms is equal to the number of different ways to divide  $N$  items into two sets, with  $n$  items in one set ("spin up") and  $N - n$  items in the other set ("spin down"):

$$W(n) = \frac{N!}{n!(N-n)!}$$

[See Appendix A.4, or the discussion on coin tossing on page 8]

\* *spin is a quantum mechanical phenomenon, but this question does not require you to know anything about it!*

To get  $W(U)$  we need to relate  $U$  to  $n$ : if  $n$  atoms are "spin up", and  $N - n$  are "spin down" then the total internal energy is

$$\begin{aligned} U(n) &= nE_0 + (N - n)(-E_0) \\ &= (2n - N)E_0 \end{aligned}$$

We can invert this expression to find  $n$  as a function of  $U$ :

$$n(U) = \frac{N}{2} + \frac{U}{2E_0}$$

and substitute it into  $W(n)$ :

$$\begin{aligned} W(U) &= \frac{N!}{\left(\frac{N}{2} + \frac{U}{2E_0}\right)! \left(\frac{N}{2} - \frac{U}{2E_0}\right)!} \\ \Rightarrow \ln W &= \ln N! - \ln \left(\frac{N}{2} + \frac{U}{2E_0}\right)! - \ln \left(\frac{N}{2} - \frac{U}{2E_0}\right)! \end{aligned}$$

To find  $T$  we need to differentiate this wrt  $U$ . To differentiate the factorial function we can use Stirling's approximation for each term because  $N$  is large (see Appendix A.6)

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

$$\begin{aligned} \Rightarrow \ln W &\approx N \ln N - \cancel{N} - \left(\frac{N}{2} + \frac{U}{2E_0}\right) \ln \left(\frac{N}{2} + \frac{U}{2E_0}\right) + \left(\cancel{\frac{N}{2}} + \cancel{\frac{U}{2E_0}}\right) \\ &\quad - \left(\frac{N}{2} - \frac{U}{2E_0}\right) \ln \left(\frac{N}{2} - \frac{U}{2E_0}\right) + \left(\cancel{\frac{N}{2}} - \cancel{\frac{U}{2E_0}}\right) \end{aligned}$$

messy; but now we can differentiate, with  $N$  and  $E_0$  constant:

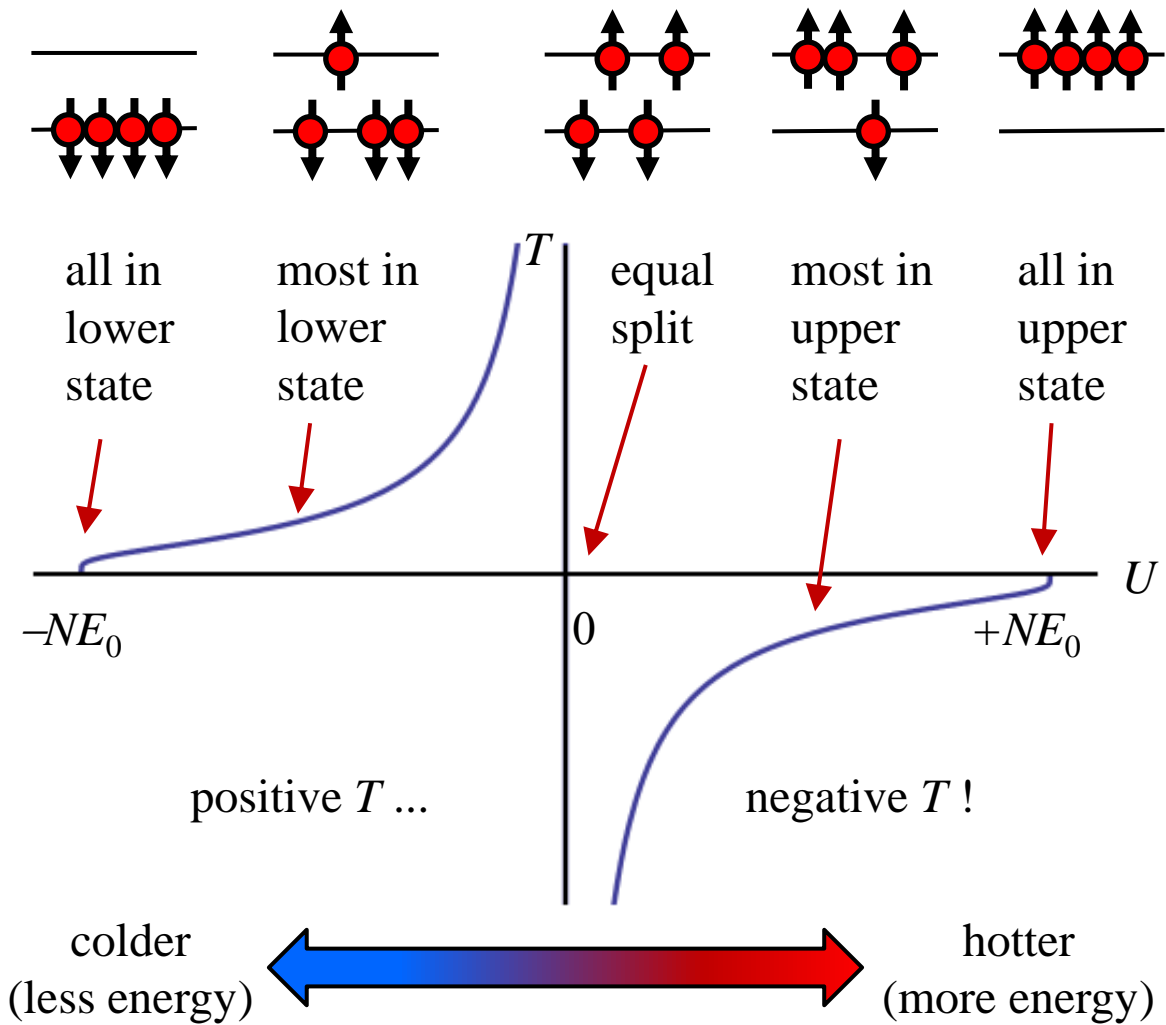
$$\begin{aligned}
 \frac{1}{k_B T} &= \frac{\partial \ln W}{\partial U} \\
 &= - \frac{\left( \frac{N}{2} + \frac{U}{2E_0} \right)}{\left( \frac{N}{2} + \frac{U}{2E_0} \right)} \left( \frac{1}{2E_0} \right) - \left( \frac{1}{2E_0} \right) \ln \left( \frac{N}{2} + \frac{U}{2E_0} \right) \\
 &\quad - \frac{\left( \frac{N}{2} - \frac{U}{2E_0} \right)}{\left( \frac{N}{2} - \frac{U}{2E_0} \right)} \left( \frac{-1}{2E_0} \right) - \left( \frac{-1}{2E_0} \right) \ln \left( \frac{N}{2} - \frac{U}{2E_0} \right)
 \end{aligned}$$

[using the product rule on each "x ln x" term]

$$= \frac{1}{2E_0} \ln \left( \frac{\frac{N}{2} - \frac{U}{2E_0}}{\frac{N}{2} + \frac{U}{2E_0}} \right) = \frac{1}{2E_0} \ln \left( \frac{NE_0 - U}{NE_0 + U} \right)$$

$$\Rightarrow T = \frac{2E_0}{k_B \ln \left( \frac{NE_0 - U}{NE_0 + U} \right)}$$

To sketch this function, you can derive approximate forms for when  $n \approx 0$  (nearly all spin "down"),  $n \approx N$  (nearly all spin "up") and  $n \approx N/2$  (roughly equal split). Instead here's a computer plot:



*Negative temperatures* are possible in closed systems with an upper bound on the SPS energy.

Negative temperatures are hotter than positive ones, and the hottest of all approaches absolute zero from below!

There is nothing paradoxical. It just means that  $\beta = 1/k_B T$  (or, better still,  $-\beta$ ) would be a much more natural and continuous way of describing how hot a system is!

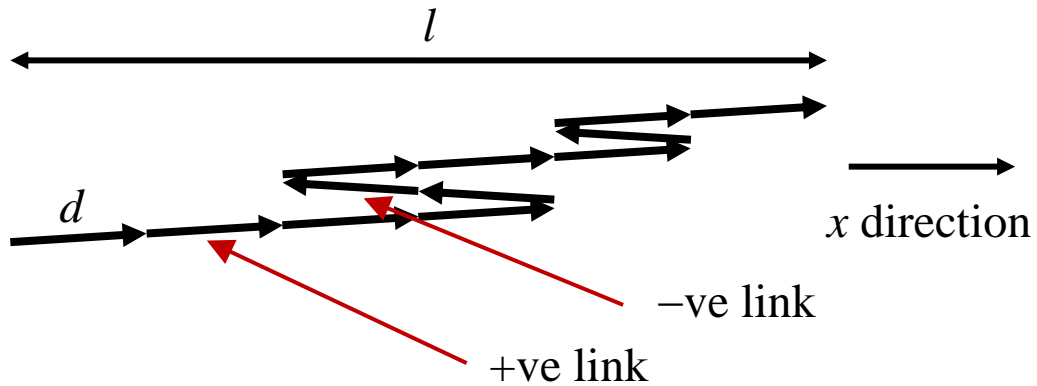
*Two-level systems - review of method*

This example was quite long and gave a surprising result, so let's review how we got there.

1. We needed to find one thermodynamic variable ( $T$ ) in terms of another ( $U$ ), and started with a "closed-system" expression (a derivative of  $\ln W$ ) linking the two.
2. Binomial statistics gave us  $W$  as a function of  $n$ , the number of atoms in one of the SPS's.
3. We could write  $W$  (and hence  $\ln W$ ) as a function of  $U$  because there was an obvious connection between  $U$  and  $n$ .
4. Stirling's approximation got rid of the factorials and made the expression differentiable.
5. The differentiation was quite messy but only needed first-year methods (product rule, chain rule, derivative of  $\ln$ ). A lot of the mess cancelled out and gave a reasonable final result.
6. Then we looked at the physics of the result and had to come to terms with negative temperatures ...

Example: rubber band

Q. Model the polymer in a rubber band as a chain of  $N$  links of length  $d$ , each of which can lie in the  $-ve$  or  $+ve$   $x$  direction. Find the tension  $F(l)$  in the band if  $N$  is large and the overall length  $l \ll Nd$ .



A. This is one of those problems where you realise that  $-pdV$  is just work done, which in a 1-D problem becomes  $-Fdl$

$$dU = TdS - Fdl \quad [1-D \text{ 1st law}]$$

$$\Rightarrow F = T \frac{\partial S}{\partial l} = k_B T \frac{\partial \ln W}{\partial l} \quad [S = k_B \ln W]$$

so we need  $W(l)$ . As with the spin system, we find  $W(n)$  from binomial statistics, with a total of  $n$  links in the  $+ve$  direction and  $N - n$  links in the  $-ve$  direction:

$$W(n) = \frac{N!}{n!(N-n)!}$$

Then with  $n$  +ve links shifting the end of the band to the right and  $N - n$  -ve links shifting it to the left, and taking the overall length to be the distance between the start and end of the band:

$$l(n) = nd + (N - n)(-d) = (2n - N)d$$

so

$$n(l) = \frac{N}{2} + \frac{l}{2d}$$

Hopefully you can see that the maths is the same as for the spin system: substitute into  $W(n)$  to get  $W(l)$ , take logs, apply Stirling's formula and differentiate messily to find  $F(l)$ :

$$F(l) = \frac{k_B T}{2d} \ln \left( \frac{Nd - l}{Nd + l} \right)$$

The Q invites us to take  $l \ll Nd$ :

$$\begin{aligned} F(l) &= \frac{k_B T}{2d} \left\{ \ln \left( 1 - \frac{l}{Nd} \right) - \ln \left( 1 + \frac{l}{Nd} \right) \right\} \\ &\approx \frac{k_B T}{2d} \left\{ -\frac{l}{Nd} - \frac{l}{Nd} \right\} \quad [\text{Taylor series for } \ln(1 + x)] \\ &= -\frac{k_B T l}{Nd^2} \end{aligned}$$

We have deduced Hooke's law ( $F \propto l$ ) and found that the tension increases with  $T$ : physical and testable predictions from a "bean counting" statistical model.

**3. System at constant temperature**(a.k.a. *canonical ensemble*)

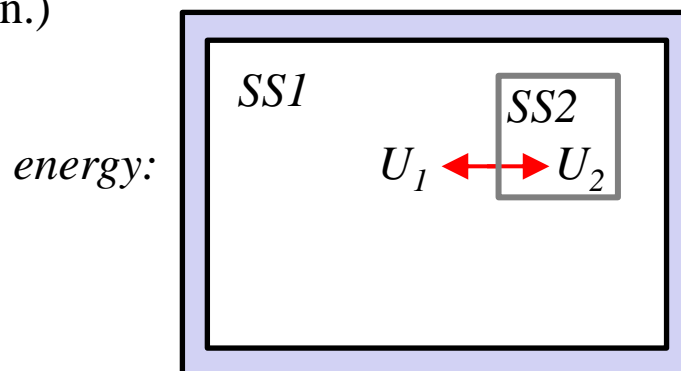
Most systems are not completely isolated (or closed): they exchange heat with their environment.

By studying such a system we will derive the Boltzmann distribution. We will spend quite some time applying it to the definitive thermodynamic system: the ideal gas.

A closed system with sub-systems SS1 and SS2 that can exchange energy (as heat) but not volume or particles. (The wall is conducting but immobile and non-porous.)

SS2 is a small system of interest.

SS1 is a *heat reservoir* or *heat bath* - so big that exchange of energy with SS2 has negligible effect on the temperature of SS1. (For example, imagine that SS2 is a pebble and SS1 is the Atlantic Ocean.)



$$\begin{array}{lcl}
 & \text{total} & U_0 = U_1 + U_2 \quad \text{fixed} \\
 \text{constant} \left\{ \begin{array}{l} \text{temperature } T \\ \text{volume } V \\ \text{no. particles } N \end{array} \right.
 \end{array}$$



Boltzmann distribution

We want to find the probability  $P(E)$  that SS2 is in a certain one of its microstates with energy  $U_2 = E$ . The statistical weight of a single microstate is by definition  $W_2(U_2) = 1$ .

We can find  $W_1(U_1)$  by integrating with  $T$  constant:

$$\left( \frac{\partial \ln W_1}{\partial U_1} \right)_{V_1, N_1} = \frac{1}{k_B T} \quad [\text{page 13}]$$

$$\ln W_1 = \frac{U_1}{k_B T} + B(V_1, N_1) \quad \left[ \begin{array}{l} \text{"constant of integration"} \\ \text{can depend on } V_1 \text{ and } N_1 \end{array} \right]$$

$$W_1(U_1) = e^{U_1/k_B T} e^B$$

The principle of equal a priori probabilities applies only to closed systems in eq<sup>m</sup>. The only closed system here is the composite system SS1+SS2. The number of accessible microstates for the composite system (when SS2 is in the chosen microstate of energy  $E$ ) is the product of the accessible microstates of the two subsystems:

$$\begin{aligned} W(E) &= W_1(U_1) \times W_2(U_2) && [\text{Appendix A.2}] \\ &= W_1(U_0 - E) \times 1 && [U_1 + U_2 = U_0; W_2 = 1] \\ &= e^B e^{U_0/k_B T} \times e^{-E/k_B T} && [W_1 \text{ from above}] \end{aligned}$$

Probability is proportional to statistical weight. Since  $U_0$ ,  $T$  and  $B$  are constant (constant  $V_1$  and  $N_1$ ):

$$P(E) \propto W(E) \propto e^{-E/k_B T}$$

or

$$P(E) = Ae^{-E/k_B T}$$

[A constant]

the *Boltzmann distribution*, a.k.a. *Maxwell-Boltzmann statistics*. (You will remember the Boltzmann factor from the Properties of Matter unit, right? Well this is where it comes from!)

This is the probability that SS2 is in a given microstate with energy  $E$ , when it is in thermal eq<sup>m</sup> at temperature  $T$ .

The constant of proportionality  $A$  is determined by the fact that the *total* probability of all the microstates of SS2 is 1:

$$\sum_{\text{all microstates } i} P(E_i) = A \sum_i e^{-E_i/k_B T} \equiv 1$$

If we define the *partition function*  $Z$  to be  $1/A$

$$Z = \sum_{\text{all microstates } i} e^{-E_i/k_B T}$$

then

$$P(E) = \frac{e^{-E/k_B T}}{Z}$$

It turns out that the partition function has more uses than just to normalise the Boltzmann distribution. For example, it is the starting point of a massive derivation (from here until page 41!) of the properties of ideal gases.

Partition function

We can use  $Z(T, V, N)$  to find all the thermodynamic variables of a system at constant temperature. (Like  $W$  for a closed system.)

• *Internal energy*


$$Z = \sum_i e^{-E_i/k_B T} \quad [\text{def}^n \text{ of } Z]$$

$$\left( \frac{\partial Z}{\partial T} \right)_{V,N} = \frac{1}{k_B T^2} \sum_i E_i e^{-E_i/k_B T} \quad [E_i \text{ constant}]$$

$$= \frac{Z}{k_B T^2} \sum_i E_i P(E_i) \quad [\text{Boltzmann distribution}]$$

$$= \frac{ZU}{k_B T^2} \quad [\sum E P(E) \equiv \text{mean of } E = U]$$

$$\Rightarrow U = k_B T^2 \frac{1}{Z} \left( \frac{\partial Z}{\partial T} \right)_{V,N}$$

  $\equiv \text{the mean of a probability dist}^n$

or 
$$U = k_B T^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{V,N}$$

• *Helmholtz free energy*

$$F = U - TS$$

[from thermodynamics]

$$dF = -SdT - pdV + \mu dN$$

$$\Rightarrow S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} \quad p = - \left( \frac{\partial F}{\partial V} \right)_{T,N} \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{T,V}$$

[chain rule for partials]

We'll use the preceding results to find the other thermodynamic variables. First the Helmholtz free energy itself:

$$U = F + TS$$

$$k_B T^2 \frac{\partial \ln Z}{\partial T} = F - T \frac{\partial F}{\partial T} \quad [\text{subst } U \text{ and } S]$$

$$= -T^2 \frac{\partial (F/T)}{\partial T} \quad [\text{work backwards!}]$$

Identify

$$F = -k_B T \ln Z$$

Now we can get everything else in terms of  $F$ :

• pressure

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \Rightarrow \boxed{p = k_B T \left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}}$$

• chemical potential

$$\mu = +\left(\frac{\partial F}{\partial N}\right)_{T,V} \Rightarrow \boxed{\mu = -k_B T \left(\frac{\partial \ln Z}{\partial N}\right)_{T,V}}$$

• entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \Rightarrow \boxed{S = k_B T \left(\frac{\partial \ln Z}{\partial T}\right)_{V,N} + k_B \ln Z}$$

Example (two level system)

Q. A two-level system has states with energies  $-E_0$  and  $+E_0$ . Find  $Z$  and hence the internal energy  $U$  and the heat capacity  $C$  of the system in eq<sup>m</sup> at temperature  $T$ .

$$\text{A. } Z = \sum_i e^{-E_i/k_B T} = e^{E_0/k_B T} + e^{-E_0/k_B T} \quad [\text{just 2 states}]$$

$$= 2 \cosh\left(\frac{E_0}{k_B T}\right)$$

$$\frac{\partial \cosh(x)}{\partial x} = \sinh(x)$$

$$U = k_B T^2 \frac{\partial \ln Z}{\partial T} = k_B T^2 \frac{\partial}{\partial T} \ln \left[ 2 \cosh\left(\frac{E_0}{k_B T}\right) \right]$$

$$= \cancel{k_B T^2} \times \frac{1}{2 \cosh(E_0 / k_B T)} \times 2 \sinh\left(\frac{E_0}{k_B T}\right) \times \left(\frac{-E_0}{\cancel{k_B T^2}}\right)$$

$$= -E_0 \tanh\left(\frac{E_0}{k_B T}\right)$$

$$\frac{\sinh(x)}{\cosh(x)} = \tanh(x)$$

$$C = \frac{dU}{dT} = -E_0 \operatorname{sech}^2\left(\frac{E_0}{k_B T}\right) \times \left(\frac{-E_0}{k_B T^2}\right)$$

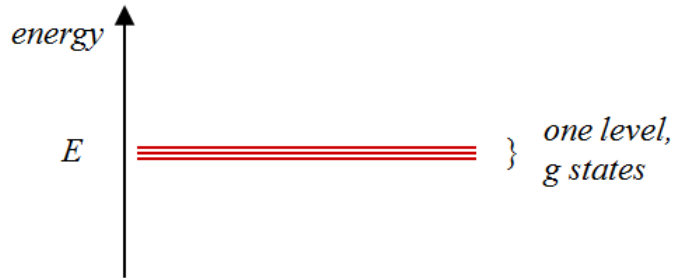
$$= \frac{E_0^2}{k_B T^2} \operatorname{sech}^2\left(\frac{E_0}{k_B T}\right)$$

$$\frac{\partial \tanh(x)}{\partial x} = \operatorname{sech}^2(x)$$

$$\operatorname{sech}(x) = 1/\cosh(x)$$

Levels and states

It's often easier to deal with *energy levels rather* than microstates. More than one microstate can have a given energy, so they share the same energy level. The number of states with a given energy  $E$  is called the *degeneracy*  $g$  of the energy level.



The probability that a system has energy  $E$  is  $g \times$  the probability of it being in any one of the states with that energy.

$$P_g(E) = g \times A e^{-E/k_B T}$$

[Boltzmann  $P(E)$ ]

Example (rotating molecule)

Q. A rotational quantum state of a molecule is defined by angular momentum quantum numbers\*  $l$  (non-negative integers) and  $m$  (integers between  $-l$  and  $+l$  inclusive) and has energy

$$E_l = \frac{l(l+1)\hbar^2}{2I}$$

where  $\hbar$  (reduced Planck's constant) and  $I$  (moment of inertia) are constants.


(a) What is the degeneracy  $g_l$  of energy level  $E_l$ ?

\* this question involves quantum mechanical angular momentum, but tells you all you need to know about it

(b) If  $\hbar^2/2I = 2 \times 10^{-21}$  J and  $T = 300$  K, what is the probability that the molecule is in the state with  $l = 3$  and  $m = 1$ , relative to the probability that it is in the state with  $l = 1$  and  $m = 1$ ?

(c) What is the probability that the molecule has energy  $E_3$ , relative to the probability that it has energy  $E_1$ ?

A. (a)  $E_l$  is independent of  $m$ , so states with the same  $l$  are degenerate. How many? For given  $l$ , list the different  $m$ :

$$m = -l, -l + 1, \dots, -1, 0, 1, \dots, l - 1, l$$


$l$  states      1 state       $l$  states

Total number of states (different  $m$ 's) is  $\boxed{g_l = 2l + 1}$

[... a general QM result for angular momentum. If you memorise nothing else about QM, memorise this! For example, spin  $s$  is a type of angular momentum and can replace  $l$ . A spin- $1/2$  level has  $g_{1/2} = 2 \times 1/2 + 1 = 2$  states: *spin up* and *spin down*.]

(b) is about states:

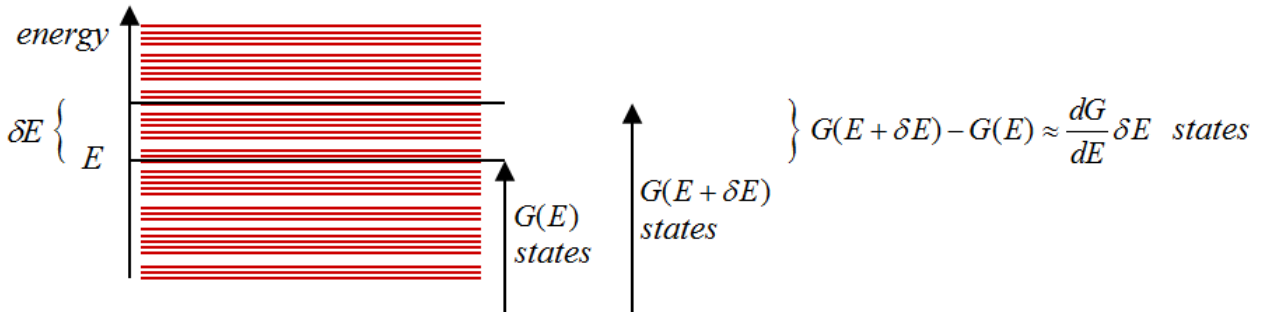
$$\begin{aligned} \frac{P(E_3)}{P(E_1)} &= \frac{\cancel{A} e^{-E_3/k_B T}}{\cancel{A} e^{-E_1/k_B T}} = e^{-(E_3 - E_1)/k_B T} \\ &= e^{-(3 \times 4 - 2 \times 1) \times 2 \times 10^{-21} / 1.38 \times 10^{-23} \times 300} = 8.0 \times 10^{-3} \end{aligned}$$

(c) is about levels:

$$\begin{aligned} \frac{P_g(E_3)}{P_g(E_1)} &= \frac{\cancel{A} g_3 e^{-E_3/k_B T}}{\cancel{A} g_1 e^{-E_1/k_B T}} = \frac{(2 \times 3 + 1)}{(2 \times 1 + 1)} \times \text{answer to (b)} \\ &= \frac{7}{3} \times 8.0 \times 10^{-3} = 1.9 \times 10^{-2} \end{aligned}$$

Continuous distributions

In big systems with closely-spaced energy levels, the states approximately form continuous *bands* rather than discrete levels. We need the equivalent of  $g$  but for continuous distributions.



Let  $G(E)$  be the number of states\* with energy  $\leq E$ . Then the number of states with energy between  $E$  and  $E + \delta E$  is

$$G(E + \delta E) - G(E) = \frac{dG}{dE} \delta E \quad [\text{def}^n \text{ of differentiation}]$$

$dG/dE$  is called the *density of states* per unit  $E$ .

Use chain rule to change variable, eg if  $E = \hbar\omega$  then the density of states per unit  $\omega$  is

$$\frac{dG}{d\omega} = \frac{dG}{dE} \frac{dE}{d\omega} = \hbar \frac{dG}{dE}$$

Partition function for a continuous distribution

The partition function is the sum of Boltzmann factors for all microstates:

$$Z = \sum_{\text{states}} e^{-E/k_B T}$$

\* Why use  $G$  (not  $N$ ) for number of states? I use  $N$  for number of particles and I don't want them to be confused! Also, some people write density of states as a function like  $g(E)$ , but I write it as a derivative  $dG/dE$  to be obvious (a) how to change variable, and (b) to multiply by  $\delta E$  to get a number of states.



For a continuous distribution, the number of states between  $E$  and  $E + \delta E$  is  $(dG/dE)\delta E$ . If *one* state contributes *one* Boltzmann factor to the sum for  $Z$ , then  $(dG/dE)\delta E$  states contribute

$$e^{-E/k_B T} \times \frac{dG}{dE} \delta E$$

Then the total partition function is the sum (but continuous  $\Rightarrow$  an *integral*) of these contributions across all energies:

$$Z = \int_0^\infty e^{-E/k_B T} \times \frac{dG}{dE} dE$$

Boltzmann factor

Density of states

Memorise?  
Maybe, but  
better to  
understand!

Example (particle in a box)

Q. Find the partition function  $Z_1$  for a single particle of mass  $m$  with  $g_I$  internal degrees of freedom in a box of volume  $V$ , given that the density of states per unit energy is

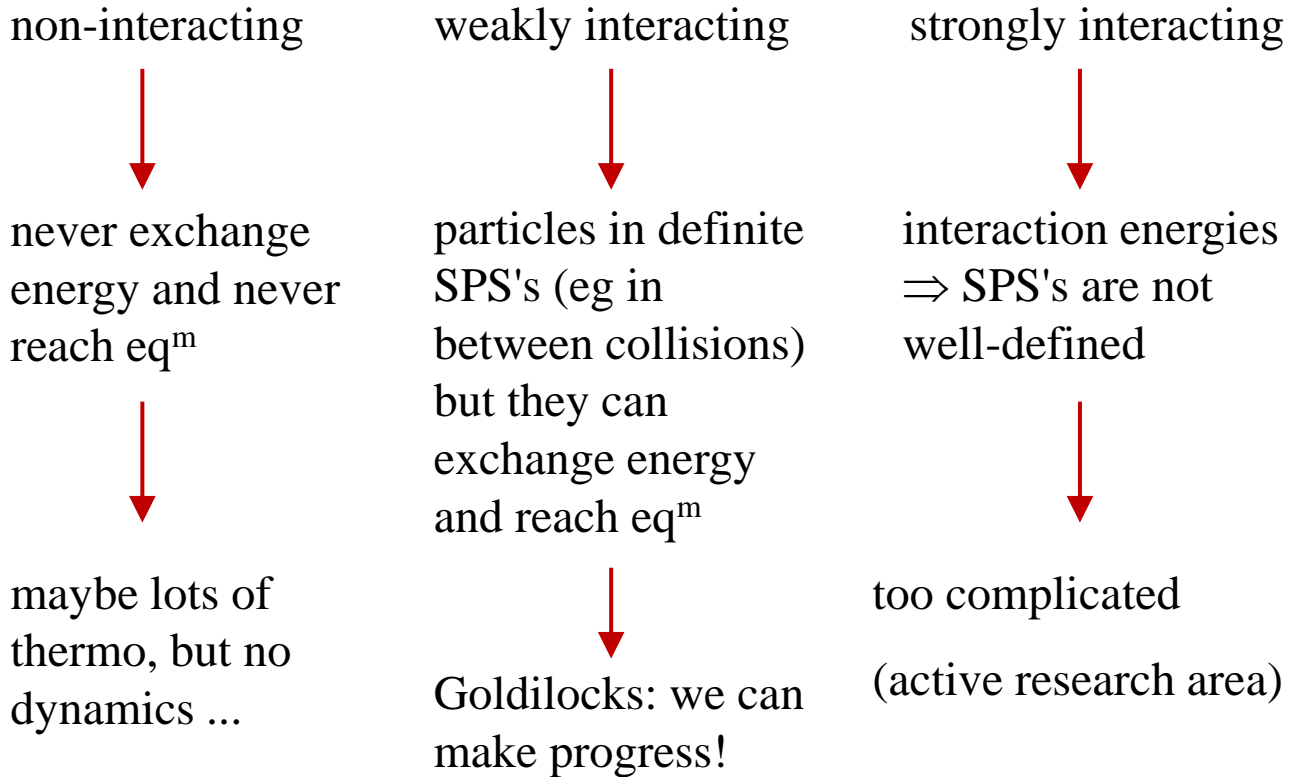
$$\frac{dG}{dE} = \frac{g_I V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} \quad [\text{Appendix B.4}]$$

$$\begin{aligned} \text{A. } Z_1 &= \int_0^\infty e^{-E/k_B T} \times \frac{dG}{dE} dE \\ &= \frac{g_I V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty E^{1/2} e^{-E/k_B T} dE \\ &= \frac{g_I V}{2\pi^2} \left( \frac{2mk_B T}{\hbar^2} \right)^{3/2} \int_0^\infty x^2 e^{-x^2} dx \quad [\text{subst } x^2 = E/k_B T] \\ &= g_I V \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \quad [\text{standard integral, Appendix C}] \end{aligned}$$

*this result, for  $Z_1$ , will be the first step in our analysis of ideal gases*

Many-particle systems

When a system contains many particles it is only profitable for us to consider the case where they are *weakly interacting*.



we can neglect interaction energies ⇒  
energy of system = sum of energies of  $N$  particles

$$E = E_1 + E_2 + \dots + E_i + \dots + E_N$$

↖ energy of the SPS that particle  $i$  is in

*it's definitely time to recall that SPS = single-particle state, a state of one particle on its own without reference to other particles*

Occupancy and number distribution

The *occupancy*  $n(E)$  of an SPS is defined to be the mean number of particles in that state. If the probability of one particle being in the state is  $P(E)$ , then

$$n(E) = N \times P(E)$$

With a continuous distribution, the mean number of particles with energy between  $E$  and  $E + \delta E$

= mean number of particles in one state  $\times$  number of states with energy between  $E$  and  $E + \delta E$

$$= n(E) \times \frac{dG}{dE} \delta E \equiv \frac{dN}{dE} \delta E \quad [\text{def}^n \text{ of } n(E) \text{ and } dG/dE]$$

where  $dN/dE$  is the *number distribution function* of the particles per unit  $E$ . The total number of particles with energy in an extended range of  $E$  can be found by integrating.

A number distribution  $dN/dE$  is normalised so that the total number of particles is  $N$ , whereas a *probability density function*  $dP/dE$  is normalised so that the total probability is 1. Hence

$$\frac{dP}{dE} = \frac{1}{N} \frac{dN}{dE}$$

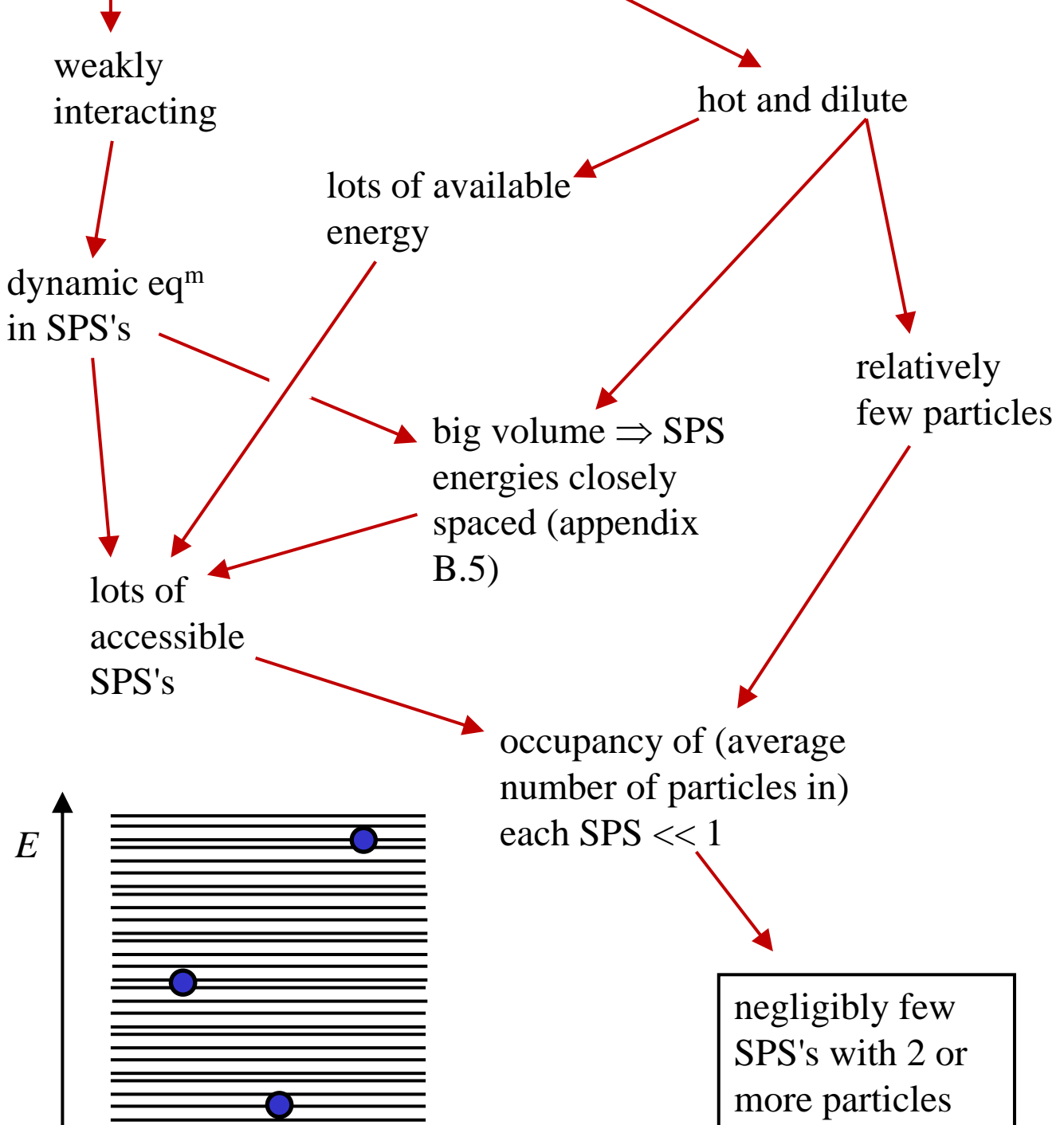
As with density of states, we can use the chain rule to change variable, eg if  $E = \hbar\omega$  then the number distribution per unit  $\omega$  is

$$\frac{dN}{d\omega} = \frac{dN}{dE} \frac{dE}{d\omega} = \hbar \frac{dN}{dE}$$

*remember and understand the definition of "occupancy"!*

Ideal classical gas

An ideal gas is a collection of many *indistinguishable* weakly-interacting particles. If the gas is hot and dilute then the quantum nature of the particles is unimportant and the gas is *classical*.



(we'll restrict ourselves to monatomic gases - no vibrational modes)

Partition function for  $N$  distinguishable particles

To derive the thermodynamics of the ideal classical gas we need its partition function  $Z_N$ .

$$Z_N = \sum_{states} e^{-E/k_B T} = \sum_{states} e^{-(E_1 + E_2 + \dots + E_N)/k_B T}$$

given that  $E$  is the sum of the energies of the particles. Assuming (falsely!) that the particles are *distinguishable* (see page 5), the microstates of the system can separately have each particle in each SPS and the sum for  $Z_N$  factorises:

$$Z_N = \sum_{\text{particle 1 SPS's}} e^{-E_1/k_B T} \times \sum_{\text{particle 2 SPS's}} e^{-E_2/k_B T} \times \dots \times \sum_{\text{particle } N \text{ SPS's}} e^{-E_N/k_B T}$$

Because the SPS's of the particles are all the same, the factors are the same and

$$\boxed{Z_N = Z_1^N}$$

[distinguishable]

where

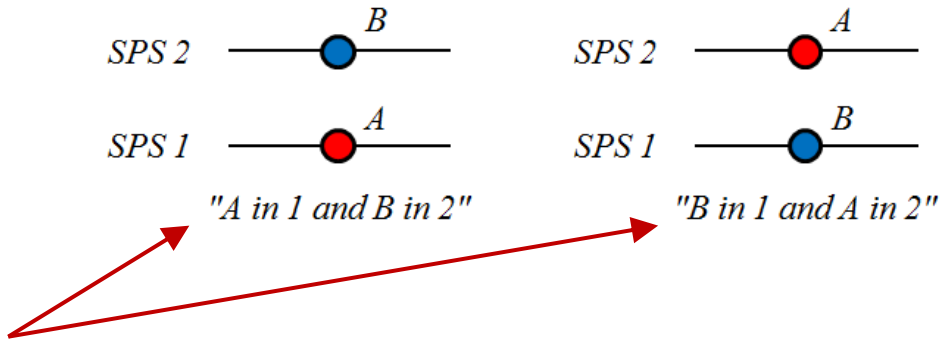
$$Z_1 = \sum_{\text{particle SPS's}} e^{-E/k_B T}$$

is the partition function for one particle on its own. (Recall that we found  $Z_1$  earlier, on page 33.)

However, the particles are in fact *indistinguishable*.

Partition function for  $N$  indistinguishable particles

The indistinguishability of the particles has a big effect on the number of microstates the system can have. Consider just two particles (A & B) and two SPS's (1 & 2):



These are two different microstates of the system if the particles are distinguishable, but they are the *same* microstate if not: "one in 1 and one in 2". Our  $Z_N$  formula

$$Z_N = Z_1^N \quad \text{[distinguishable]}$$

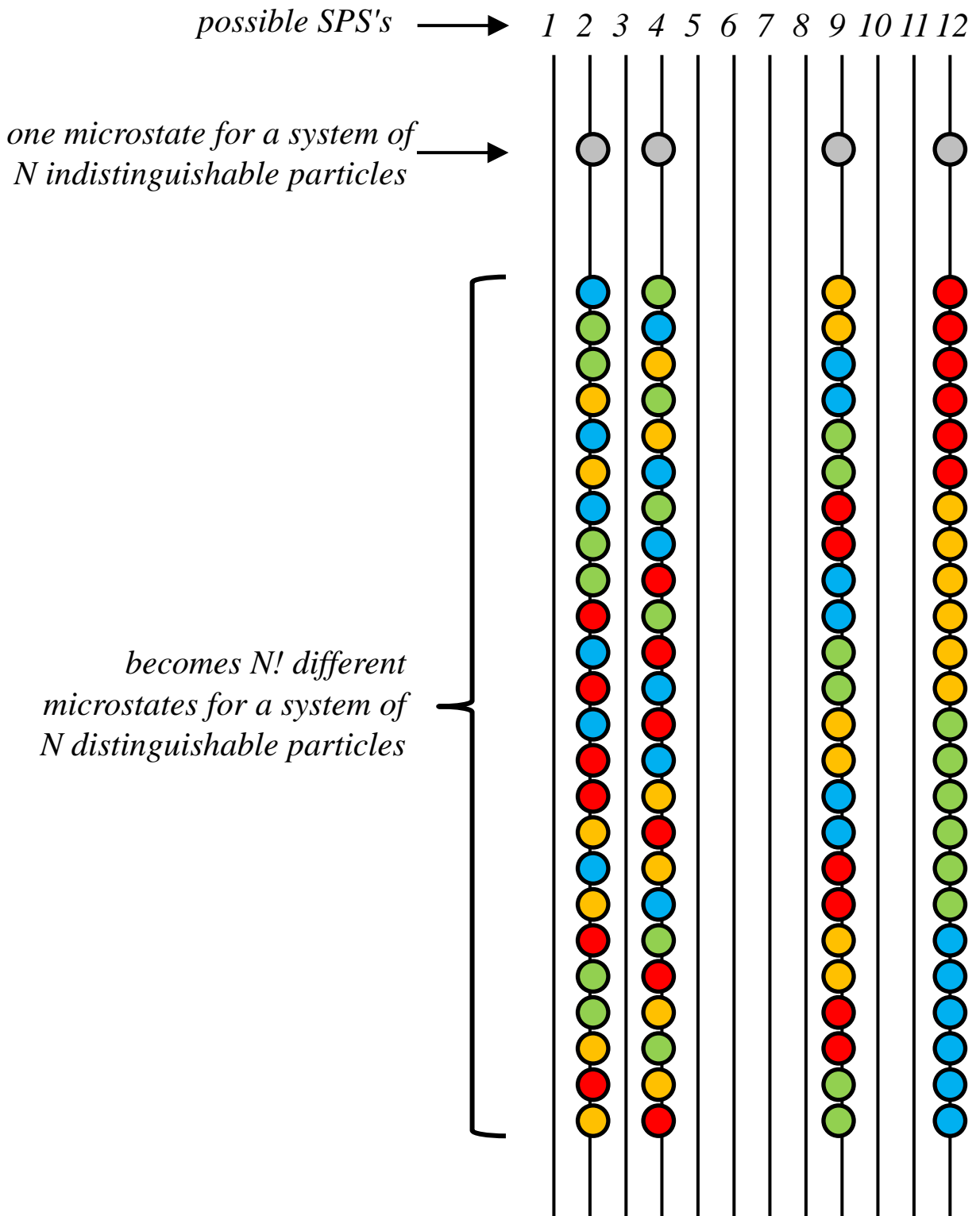
therefore *overcounts* the number of microstates - we summed over many microstates that were in fact the same.

Classical gas: no SPS's containing 2 or more particles  
 $\Rightarrow N$  particles in  $N$  different SPS's.

There are  $N!$  ways to arrange  $N$  *distinguishable* particles among  $N$  SPS's ( $N!$  ordered lists - see Appendix A3), but for *indistinguishable* particles these are all the same microstate (1 unordered list). The  $Z_N$  formula therefore overcounts by a factor of  $N!$

$$\boxed{Z_N = \frac{Z_1^N}{N!}} \quad \text{[indistinguishable]}$$

Illustration for  $N = 4$ :



(the  $N!$  factor assumes no SPS is occupied by two or more particles - ie, only for a classical gas)

Thermodynamics of the ideal classical gas

Now we can finally write down the partition function for the classical gas, and hence all of its thermodynamic variables.

For a single particle in a box we found

$$Z_1 = g_I V \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}$$

so

$$Z_N = \frac{Z_1^N}{N!} = \frac{(g_I V)^N}{N!} \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3N/2}$$

$$\ln Z_N = N \ln Z_1 - \ln N!$$

$$\approx N \ln(g_I V) + \frac{3N}{2} \ln \left( \frac{mk_B T}{2\pi\hbar^2} \right) - N \ln N + N \quad [\text{Stirling's}]$$

$$= N \left[ \ln \left( \frac{g_I V}{N} \right) + \frac{3}{2} \ln T + \frac{3}{2} \ln \left( \frac{mk_B}{2\pi\hbar^2} \right) + 1 \right]$$

$$\bullet \quad U = k_B T^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{V,N} = k_B T^2 \times \frac{3N}{2T} = \frac{3}{2} N k_B T$$

$$\text{or} \quad U = \frac{3}{2} n R T$$

$$\text{where} \quad N k_B = n \times N_A k_B = n R$$

$n$  = number of moles

$N_A$  = Avogadro's number

$R$  = molar gas constant



## Lecture 6

- $$p = k_B T \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N} = k_B T \times \frac{N}{V}$$

or  $\boxed{pV = nRT}$

the equation of state of an ideal gas: "ideal gas law"

- $$S = k_B T \left( \frac{\partial \ln Z}{\partial T} \right)_{V,N} + k_B \ln Z$$

$$\Rightarrow \boxed{S = Nk_B \left[ \ln \left( \frac{g_I V}{N} \right) + \frac{3}{2} \ln \left( \frac{mk_B T}{2\pi\hbar^2} \right) + \frac{5}{2} \right]}$$

the *Sackur-Tetrode equation*: for the first time, a closed-form expression for the entropy of an ideal gas!

Note that it contains Planck's constant  $\hbar$  - this result cannot be obtained using classical physics.

Note also that  $S$  is an extensive variable  $\propto N$ , as it should be (given that  $N/V$  is concentration, an intensive variable).

Derivation from  $Z_N = Z_1^N$  gives a non-extensive (and therefore wrong) answer - see problem sheet 2 Q 10.

Indistinguishability is important and has real-world physical consequences!

- $$\mu = -k_B T \left( \frac{\partial \ln Z}{\partial N} \right)_{T,V}$$

$$\Rightarrow e^{-\mu/k_B T} = \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \frac{g_I V}{N}$$

(see problem sheet 2 Q 8)

Example (Joule expansion)

Q. A wall divides a box into sections 1 and 2, each of volume  $V_0$ . X and Y are different ideal gases. The sections contain:

|     | section 1          | section 2          |
|-----|--------------------|--------------------|
| (a) | $N$ particles of X | nothing            |
| (b) | $N$ particles of X | $N$ particles of Y |
| (c) | $N$ particles of X | $N$ particles of X |

In each case, what is the change of entropy after the wall is removed and the contents are allowed to reach eq<sup>m</sup>?

A. Energy  $U = \frac{3}{2} Nk_B T$  conserved  $\Rightarrow T$  constant.

Sackur-Tetrode:

$$S = Nk_B \left[ \ln \left( \frac{g_I V}{N} \right) + \frac{3}{2} \ln \left( \frac{mk_B T}{2\pi\hbar^2} \right) + \frac{5}{2} \right]$$

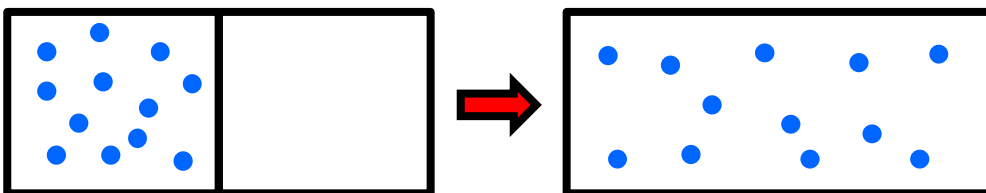
$$= Nk_B \ln \left( \frac{V}{N} \right) + N\alpha$$

where  $\alpha$  is a constant for a given gas.

(a) before:  $S = Nk_B \ln(V_0 / N) + N\alpha_X$  [ $N \times X$  in volume  $V_0$ ]

after:  $S' = Nk_B \ln(2V_0 / N) + N\alpha_X$  [ $N \times X$  in volume  $2V_0$ ]  
 $= Nk_B \ln 2 + Nk_B \ln(V_0 / N) + N\alpha_X$

$$\Rightarrow \Delta S = S' - S = Nk_B \ln 2$$

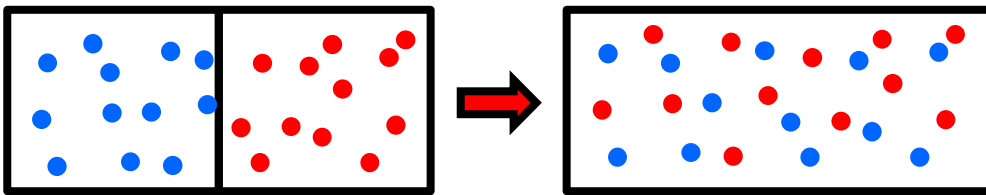


[Joule expansion: irreversible  $\Delta S > 0$ ]

(b) before:  $S = Nk_B \ln(V_0 / N) + N\alpha_X$  [N×X in volume  $V_0$ ]  
 $+ Nk_B \ln(V_0 / N) + N\alpha_Y$  [N×Y in volume  $V_0$ ]

after:  $S' = Nk_B \ln(2V_0 / N) + N\alpha_X$  [N×X in volume  $2V_0$ ]  
 $+ Nk_B \ln(2V_0 / N) + N\alpha_Y$  [N×Y in volume  $2V_0$ ]  
 $= Nk_B \ln 2 + Nk_B \ln(V_0 / N) + N\alpha_X$   
 $+ Nk_B \ln 2 + Nk_B \ln(V_0 / N) + N\alpha_Y$

$\Rightarrow \Delta S = 2Nk_B \ln 2$

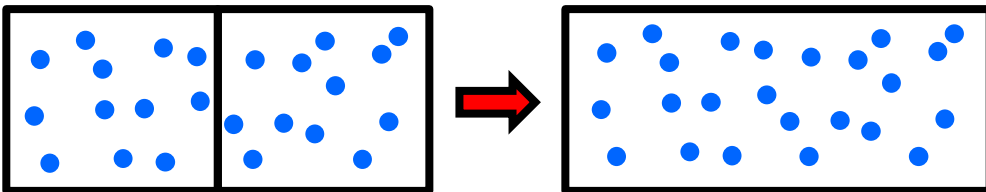


[2 diffusive  
expansions:  
irreversible  
 $\Delta S > 0$ ]

(c) before:  $S = Nk_B \ln(V_0 / N) + N\alpha_X$  [N×X in volume  $V_0$ ]  
 $+ Nk_B \ln(V_0 / N) + N\alpha_X$  [N×X in volume  $V_0$ ]

after:  $S' = 2Nk_B \ln(2V_0 / 2N) + 2N\alpha_X$  [2N×X in volume  $2V_0$ ]  
 $= 2Nk_B \ln(V_0 / N) + 2N\alpha_X$

$\Rightarrow \Delta S = 0$



[no change:  
reversible  
 $\Delta S = 0$ ]

Case (c) is reversible - we can put the wall back and recover the initial conditions. Since the particles of gas X are indistinguishable, we have no way of telling which particles were originally in which section.

### Equipartition theorem

The *equipartition of energy theorem* states that each quadratic degree of freedom of a thermodynamic system in eq<sup>m</sup> contributes an average of  $\frac{1}{2}k_B T$  to the internal energy.

This is only true if  $\frac{1}{2}k_B T$  is large compared to the splitting between the quantum energy levels - it is a classical result. However, for us it provides a useful check for high-temperature limits.

For example, each particle in an ideal classical gas of  $N$  particles has 3 degrees of freedom for translational motion (ie, in the  $x$ ,  $y$  and  $z$  directions). The equipartition theorem then says that the internal energy should be  $N \times 3 \times \frac{1}{2}k_B T$ , or

$$U = \frac{3}{2} N k_B T$$

This is exactly what we found from the partition function earlier.

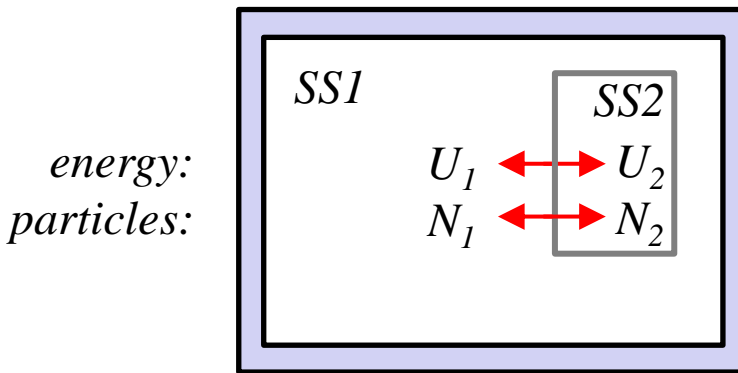
**4. System at constant  $T$  and  $\mu$** (a.k.a. *grand canonical ensemble*)

By studying this system we will derive the Gibbs distribution and apply it to ideal quantum (fermion and boson) gases.

A closed system with sub-systems SS1 and SS2 that can exchange energy and particles but not volume. (The wall is conducting and porous but immobile.)

SS2 is a small system of interest.

SS1 is a *heat and particle reservoir* - so big that exchange of energy and particles with SS2 has negligible effect on the temperature and chemical potential of SS1.



$$\text{total} \left\{ \begin{array}{l} U_0 = U_1 + U_2 \\ N_0 = N_1 + N_2 \end{array} \right\} \text{fixed}$$

$$\text{constant} \left\{ \begin{array}{l} \text{temperature } T \\ \text{volume } V \\ \text{chemical potential } \mu \end{array} \right.$$

Gibbs distribution

The following derivation is a generalisation of the one for the Boltzmann distribution.

We want to find the probability  $P(E_i, n_i)$  that SS2 is in a certain one of its microstates with energy  $U_2 = E_i$  and number of particles  $N_2 = n_i$ . By definition  $W_2(U_2, N_2) = 1$ .

We can find  $W_1(U_1)$  by integrating with  $T$  constant:

$$\left( \frac{\partial \ln W_1}{\partial U_1} \right)_{V_1, N_1} = \frac{1}{k_B T} \quad [\text{page 13}]$$

$$\ln W_1 = \frac{U_1}{k_B T} + B(V_1, N_1) \quad \left[ \begin{array}{l} \text{"constant of integration"} \\ \text{can depend on } V_1 \text{ and } N_1 \end{array} \right]$$

and integrating with  $T$  and  $\mu$  constant:

$$\left( \frac{\partial \ln W_1}{\partial N_1} \right)_{U_1, V_1} = -\frac{\mu}{k_B T} \quad [\text{page 14}]$$

$$\ln W_1 = -\frac{\mu N_1}{k_B T} + C(U_1, V_1) \quad \left[ \begin{array}{l} \text{"constant of integration"} \\ \text{can depend on } U_1 \text{ and } V_1 \end{array} \right]$$

The expressions for  $\ln W_1$  are consistent if

$$\ln W_1 = \frac{U_1}{k_B T} - \frac{\mu N_1}{k_B T} + D(V_1) \quad \left[ \begin{array}{l} \text{"constant of integration"} \\ \text{can depend on } V_1 \end{array} \right]$$

$$W_1(U_1, N_1) = e^{U_1/k_B T} e^{-\mu N_1/k_B T} e^D$$

Then the statistical weight for the composite system is

$$\begin{aligned}
 W(E, n) &= W_1(U_1, n_1) \times W_2(U_2, n_2) && [\text{Appendix A.2}] \\
 &= W_1(U_0 - E_i, N_0 - n_i) \times 1 && [\text{total } U_0 \text{ \& } N_0; W_2 = 1] \\
 &= e^D e^{U_0/k_B T} e^{-\mu N_0/k_B T} \times e^{-E_i/k_B T} e^{\mu n_i/k_B T} && [W_1 \text{ from above}]
 \end{aligned}$$

Probability is proportional to statistical weight. Since  $U_0$ ,  $N_0$ ,  $T$  and  $D$  are constant (constant  $V_1$ ):

$$P(E_i, n_i) \propto W(E_i, n_i) \propto e^{(\mu n_i - E_i)/k_B T}$$

or

$$\boxed{P(E_i, n_i) = \frac{e^{(\mu n_i - E_i)/k_B T}}{\Xi}} \quad [\Xi = \text{Greek capital "xi"}]$$

the *Gibbs* or *grand canonical distribution*. This is the probability that SS2 is in a given microstate with energy  $E_i$  and number of particles  $n_i$ , when it is in thermal eq<sup>m</sup> with a heat and particle reservoir at temperature  $T$  and chemical potential  $\mu$ .

Total probability = 1 gives the *grand partition function*  $\Xi$

$$\boxed{\Xi = \sum_{\text{all microstates } i} e^{(\mu n_i - E_i)/k_B T}}$$

We will use the Gibbs distribution for just one specialist purpose: to analyse *quantum gases*.

### Ideal quantum gas

If an ideal gas is "cold and dense" then there are few accessible SPS's compared to the number of particles to occupy them (in contrast to the "hot and dilute" ideal classical gas of page 36). We must consider the possibility of more than one particle occupying the same SPS, depending on *the quantum nature of the particles*.

We use the Gibbs distribution, where:

SS2 is the set of particles in one SPS with energy  $E$ . If there are  $n_i = n$  of these particles, the total energy in SS2 is  $E_i = nE$ .

SS1 is all the other particles, acting as a heat and particle reservoir for SS2 with constant  $T$  and  $\mu$ .

There are two types of quantum particle: *fermions* and *bosons*, depending on whether or not the particle obeys the *Pauli exclusion principle*.

The Pauli exclusion principle states that two (or more) identical particles cannot occupy the same SPS.


What determines whether a particle is a fermion or a boson is its *spin*. This is the most fundamental distinction between particles, and gives rise to quite different statistical properties. (Why angular momentum should have such a profound effect on statistics is a bit of a mystery: the *spin-statistics theorem* has no simple proof.)



Fermions

A fermion is any particle with half-odd-integer spin:

$s = 1/2, 3/2, 5/2, \dots$  (eg, electrons, protons,  $^3\text{He}$  nuclei)

Fermions obey the *Pauli exclusion principle*: two (or more) identical fermions cannot occupy the same SPS. 

Our small system therefore has *only two microstates*,  $n = 0$  or  $1$ :  
 either  $n_i = 0, E_i = 0$  (no fermion in this SPS)  
 or  $n_i = 1, E_i = E$  (one fermion in this SPS)

The *occupancy\** of the SPS is

$$\begin{aligned}
 n_{FD} &= \sum_{\text{all microstates } i} n_i P(E_i, n_i) && [\text{def}^n \text{ of average } n] \\
 &= \frac{\sum_{n=0}^1 n e^{(n\mu - nE)/k_B T}}{\sum_{n=0}^1 e^{(n\mu - nE)/k_B T}} && [\text{Gibbs dist}^n P(E_i, n_i)] \\
 &\quad \text{maximum } n \rightarrow \quad \quad \quad \Xi \\
 &= \frac{0 \times 1 + 1 \times e^{(\mu - E)/k_B T}}{1 + e^{(\mu - E)/k_B T}} && \text{now } \div \text{ by the exponential} \\
 \Rightarrow \quad &\boxed{n_{FD}(E) = \frac{1}{e^{(E - \mu)/k_B T} + 1}}
 \end{aligned}$$

the *Fermi-Dirac distribution function* - the average number of fermions in a single-particle state of energy  $E$ .

$\mu$  normalises the distribution so that  $\sum_{\text{all SPS's}} n_{FD}(E) = N$ , the total number of particles.


$\mu$  is also the value of  $E$  such that an SPS has a 50% chance of being occupied:  $n_{FD}(\mu) = 1/2$ . (Note that  $n_{FD} \leq 1$  for all  $E$ .)

\* remember that "occupancy of" = average number of particles in

Bosons

A boson is any particle with integer spin:

$s = 0, 1, 2, \dots$  (eg, photons, phonons,  $^4\text{He}$  nuclei)

Bosons *do not* obey the Pauli exclusion principle: *any* number of identical bosons can occupy the same SPS. 

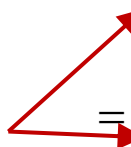
Our small system therefore has an *infinite number of microstates*,  $n = 0, 1, 2, \dots$

the  $n$ -th microstate:  $n_i = n, E_i = nE$  ( $n$  bosons in this SPS)


The occupancy of the SPS is

$$n_{BE} = \sum_{\text{all microstates } i} n_i P(E_i, n_i) \quad [\text{def}^n \text{ of average } n]$$

$$= \frac{\sum_{n=0}^{\infty} n e^{(n\mu - nE)/k_B T}}{\sum_{n=0}^{\infty} e^{(n\mu - nE)/k_B T}} \quad [\text{Gibbs dist}^n P(E_i, n_i)]$$


$n$  unlimited 

$$= \frac{e^{(\mu - E)/k_B T}}{\left[1 - e^{(\mu - E)/k_B T}\right]^2} \times \left[1 - e^{(\mu - E)/k_B T}\right] \quad [\text{sums from Appendix D}]$$

$$\Rightarrow \boxed{n_{BE}(E) = \frac{1}{e^{(E - \mu)/k_B T} - 1}} \quad \begin{array}{l} \text{[only difference cf FD:} \\ \text{– instead of +]} \end{array}$$


the *Bose-Einstein distribution function* - the average number of bosons in a single-particle state of energy  $E$ .

$\mu$  normalises the distribution so that  $\sum_{\text{all SPS's}} n_{BE}(E) = N$ , the total number of particles.

$\mu$  must be less than the lowest ("ground state") energy  $E$ , to avoid unphysical infinite or negative occupancies  $n_{BE}$ .  
(Note that  $n_{BE}$  can take any positive value for  $E > \mu$ .) 

The classical regime

How can we tell if an ideal gas is classical or quantum? Saying that a classical gas is "hot and dilute" is not quantitative enough!

Our treatment of the ideal classical gas assumed occupancy  $n(E) \ll 1$  and a negligible chance of two particles trying to share one SPS. In that case, whether the particles are fermions or bosons is irrelevant.

$$n(E) = \begin{cases} n_{FD}(E) \\ n_{BE}(E) \end{cases} = \frac{1}{e^{(E-\mu)/k_B T} \pm 1} \ll 1$$

[classical gas]  
[upper sign FD;  
lower sign BE]

$$\Rightarrow e^{(E-\mu)/k_B T} \gg 1$$

[both cases]

in which case  $n(E) \propto e^{-E/k_B T}$

$\Rightarrow$  both FD and BE reduce to the Boltzmann distribution.

Criterion for a classical gas

Since all  $E$  for a particle in a box are positive but the ground state  $E$  is very close to zero (Appendix B.5), it is sufficient that

$$e^{-\mu/k_B T} \gg 1$$

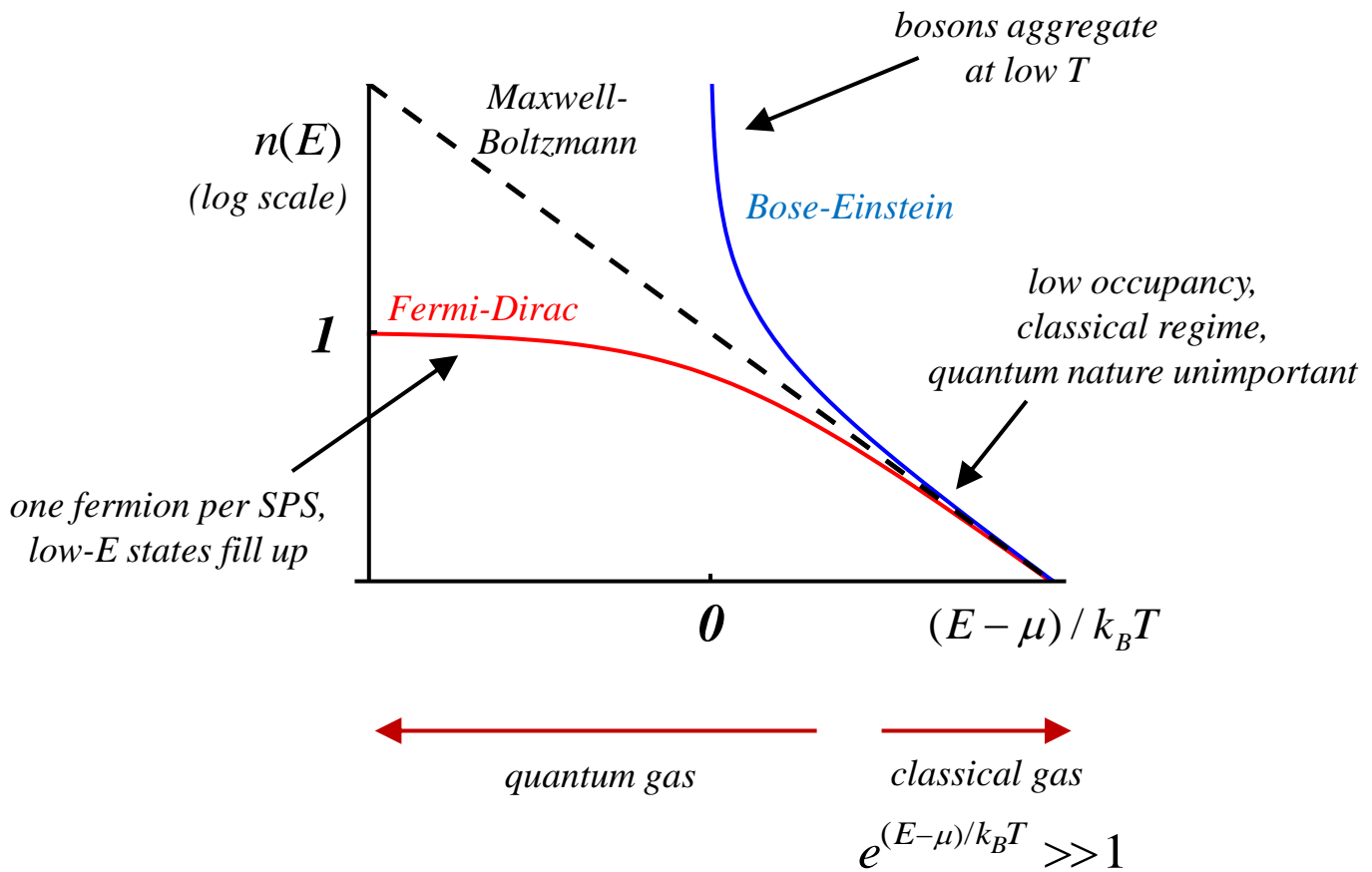
but for an ideal classical gas (see page 41):

$$e^{-\mu/k_B T} = \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} \frac{g_I V}{N}$$

So an ideal gas is classical if

$$\frac{N}{g_l V} \left( \frac{2\pi\hbar^2}{mk_B T} \right)^{3/2} \ll 1$$

ie, for high temperatures  $T$  and/or low concentrations  $N/V$ :  
"hot and dilute".



If the ideal gas does not satisfy the criterion for a classical gas, we must consider the fermion and boson cases separately.

Ideal fermion gas

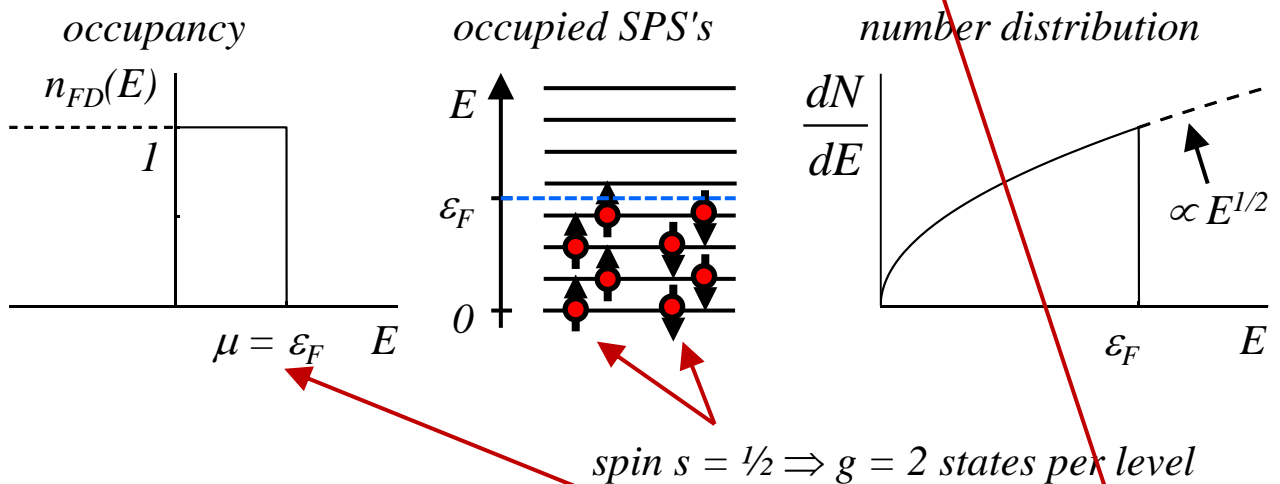
eg, free electrons in metals, electrons in white dwarf stars,  
(also related: atoms in helium-3, neutrons in neutron stars)

Look at occupancy  $n_{FD}$  and number distribution  $dN/dE$  at different temperatures  $T$ , recalling that

$$\begin{aligned} \frac{dN}{dE} &= n_{FD}(E) \frac{dG}{dE} && [\text{density of states } dG/dE] \\ &= \frac{g_I}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} V E^{1/2} n_{FD}(E) && [\text{particle in a box}] \end{aligned}$$

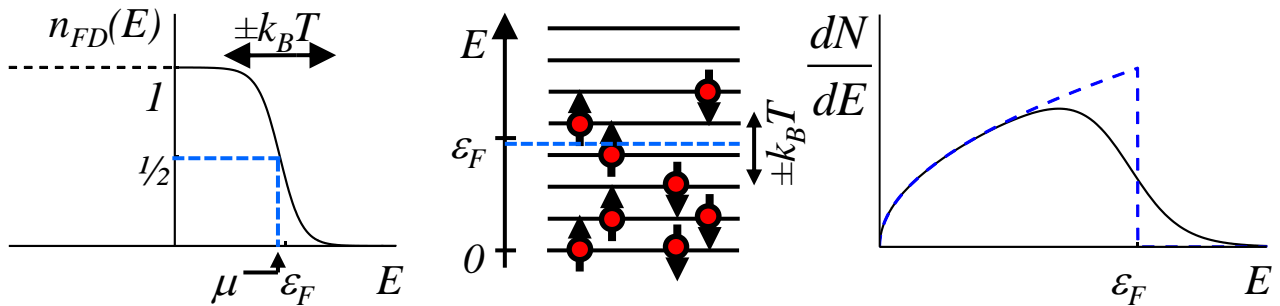
- absolute zero,  $T \rightarrow 0$ , "completely degenerate fermion gas"

$$n_{FD}(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1} \quad \xrightarrow{T \rightarrow 0} \quad \begin{cases} 1 & E < \mu \\ 0 & E > \mu \end{cases}$$



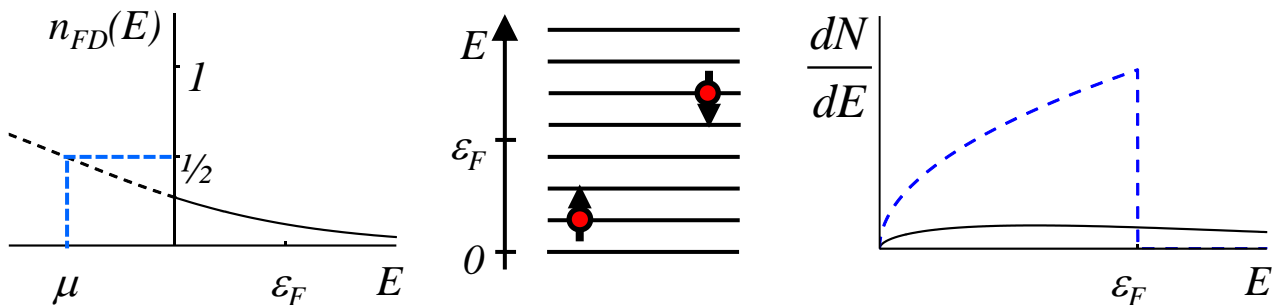
All SPS's up to  $E = \mu$  are fully occupied, the rest are empty. The chemical potential  $\mu$  at  $T \rightarrow 0$  is called the *Fermi energy*  $\epsilon_F$ , with the *Fermi temperature*  $T_F$  defined by  $\epsilon_F = k_B T_F$ .

- cold,  $T \ll T_F$ , "degenerate fermion gas"



Still  $\mu \approx \epsilon_F$ , but slightly smaller. Some particles are excited from SPS's below  $\epsilon_F$  to SPS's above  $\epsilon_F$ . This mainly affects states within  $\sim k_B T$  of  $\epsilon_F$ . If  $|E - \mu| \gg k_B T_F$ ,  $n_{FD}(E)$  remains close to 0 or 1\*.

- hot,  $T \gg T_F$ , "classical fermion gas"



All occupancies are small (certainly less than  $1/2$ ) so  $\mu$  becomes negative.  $n_{FD}(E)$  becomes the Boltzmann distribution.

\* don't take my word for it - check for yourself from  $n_{FD}(E)$ !

Thermodynamic variables

- chemical potential  $\mu$

We find  $\mu$  by normalising the number distribution  $dN/dE$ :

$$\begin{aligned} N &= \int_0^\infty \frac{dN}{dE} dE \\ &= \int_0^\infty \frac{g_I}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} V E^{1/2} n_{FD}(E) dE \end{aligned}$$

This can be solved for  $\mu$ , which appears on the RHS inside the expression for  $n_{FD}(E)$ . However, the integral can't be found analytically so in general a numerical solution is needed.

- Fermi energy  $\varepsilon_F$  ( $\mu$  as  $T \rightarrow 0$ )

However, we can integrate as  $T \rightarrow 0$  because  $n_{FD}(E)$  simplifies:

$$n_{FD}(E) \rightarrow \begin{cases} 1 & E < \varepsilon_F \\ 0 & E > \varepsilon_F \end{cases} \quad [T \rightarrow 0]$$

$$\begin{aligned} \Rightarrow N &= \int_0^{\varepsilon_F} \frac{g_I}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} V E^{1/2} dE \\ &= \frac{g_I}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} V \times \frac{2}{3} \left[ E^{3/2} \right]_0^{\varepsilon_F} \\ &= \frac{g_I}{6\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} V \varepsilon_F^{3/2} \end{aligned}$$

$$\Rightarrow \varepsilon_F = \left( \frac{6\pi^2}{g_I} \frac{N}{V} \right)^{2/3} \frac{\hbar^2}{2m} \quad \begin{array}{l} \text{[cf classical gas:} \\ \mu \rightarrow 0 \text{ as } T \rightarrow 0] \end{array}$$

- internal energy  $U$  (as  $T \rightarrow 0$ )

Again, the functional form of  $n_{FD}(E)$  means we can only perform our integrals as  $T \rightarrow 0$ .

Evaluate the sum of particle energies  $E$ , given  $(dN/dE)\delta E$  particles in energy range  $\delta E$ :

$$U = \int_0^\infty E \left( \frac{dN}{dE} \right) dE$$

= ...

[missing steps:  
problem sheet 3 Q 2]

$$= \frac{g_I}{10\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} V \varepsilon_F^{5/2}$$

Use our expression for  $\varepsilon_F$  to eliminate  $\hbar$ ,  $m$ , etc:

$$U = \frac{3}{5} N \varepsilon_F \quad [T \rightarrow 0]$$

[cf classical gas:  
 $U \rightarrow 0$  as  $T \rightarrow 0$ ]

Unlike in a classical gas,  $U$  is finite even as  $T \rightarrow 0$ , because the Pauli exclusion principle forces particles into states well above the ground state.

- pressure  $p$  (as  $T \rightarrow 0$ )

$$p = - \left( \frac{\partial U}{\partial V} \right)_{S,N}$$

thermodynamics: from  $dU = \dots$

= ...

[\*missing steps:  
problem sheet 3 Q 2]

$$= \frac{2}{5} \frac{N}{V^{5/3}} \left( \frac{6\pi^2 N}{g_I} \right)^{2/3} \frac{\hbar^2}{2m}$$

\* while differentiating, note that  $\varepsilon_F$  depends on  $V$



Again use our expression for  $\varepsilon_F$  to eliminate  $\hbar$ ,  $m$ , etc:

$$p = \frac{2}{5} \frac{N}{V} \varepsilon_F \quad [T \rightarrow 0] \quad \begin{array}{l} \text{[cf classical gas:} \\ p \rightarrow 0 \text{ as } T \rightarrow 0] \end{array}$$

Unlike in a classical gas,  $p$  is finite even as  $T \rightarrow 0$ , because the Pauli exclusion principle resists attempts to compress fermions into a smaller volume. Indeed this *degeneracy pressure* is what stops white dwarf and neutron stars collapsing under gravity and forming black holes!

Ideal boson gas

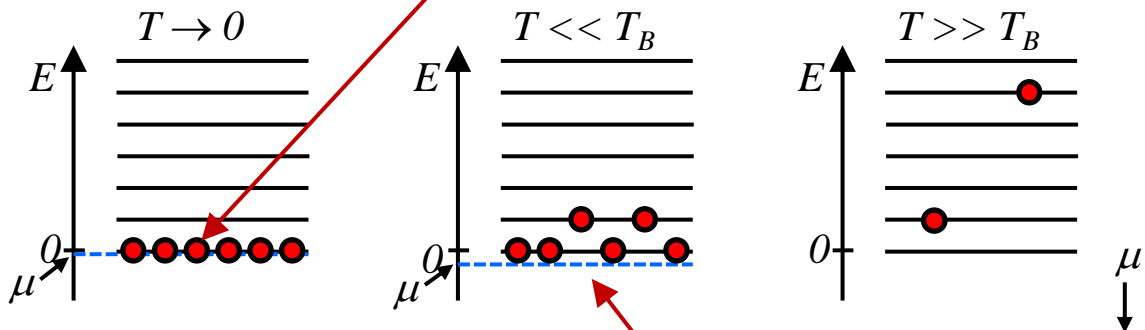
eg, photons in a black-body cavity, phonons in a solid,  
(also related: atoms in helium-4)

- absolute zero,  $T \rightarrow 0$ , "completely degenerate boson gas"

All  $N$  particles are in the ground state ( $E = 0$ ):

$$n_{BE}(E) = \frac{1}{e^{(E-\mu)/k_B T} - 1} \quad \xrightarrow{T \rightarrow 0} \quad \begin{cases} N & E = 0 \\ 0 & E > 0 \end{cases}$$

This limit requires  $\mu$  to be just below  $E = 0$ .



- cold,  $T \ll T_B$ , "degenerate boson gas"

Some particles are excited out of the ground state, but a large fraction of them (ie, a *macroscopic* number) remain there. The *Bose temperature*  $T_B$  is the temperature below which the ground state population is macroscopic. The formation of a macroscopic ground state population is called *Bose-Einstein condensation*.

- hot,  $T \gg T_B$ , "classical boson gas"

See classical fermion gas.  $n_{BE}(E) \rightarrow$  Boltzmann distribution.

Radiation

Consider a *photon gas* with volume  $V$  and internal energy  $U$  in thermal eq<sup>m</sup> at temperature  $T$ . Unlike many other particles, photons can be readily created and destroyed: photon number is *not conserved*. Consider variable  $N$  while  $U$  and  $V$  are fixed:

$$dU = TdS - pdV + \mu dN$$

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

But  $S$  is maximised at eq<sup>m</sup>, so

$$\left( \frac{\partial S}{\partial N} \right)_{U,V} = 0$$

$\Rightarrow \mu = 0$  for non-conserved particles.

Photons have spin  $s = 1$  so they are bosons, and the occupancy of a photon SPS is the Bose-Einstein distribution function with  $E = \hbar\omega$  and  $\mu = 0$ :

$$n(\omega) = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

The photon density of states per unit  $\omega$  is

$$\frac{dG}{d\omega} = \frac{V\omega^2}{\pi^2 c^3}$$

[Appendix B.4]

The mean number of photons between  $\omega$  and  $\omega + \delta\omega$  is

$$\delta n = n(\omega) \frac{dG}{d\omega} \delta\omega \quad [\text{number distribution} = n \, dG/d\omega]$$

The mean photon energy between  $\omega$  and  $\omega + \delta\omega$  is

$$\delta E = \hbar\omega \times \delta n \quad [\text{each photon } E = \hbar\omega]$$

Putting all this together, the mean *energy density* (energy per unit volume) for the photons between  $\omega$  and  $\omega + \delta\omega$  is

$$\frac{1}{V} \frac{dE}{d\omega} \equiv \frac{du}{d\omega} = \frac{\hbar\omega^3}{\pi^2 c^3 \left[ e^{\hbar\omega/k_B T} - 1 \right]} \quad [\text{energy density } u \equiv E/V]$$

### ● Radiated intensity

From the kinetic theory of gases, the *number of particles* striking a wall per unit time per unit area is  $\frac{1}{4}nv$ , where  $n$  is the *number density* of the particles and  $v$  is their mean speed.

By analogy, the *photon energy per unit range of  $\omega$*  striking a wall per unit time per unit area is

$$\frac{1}{4} \frac{du}{d\omega} c$$

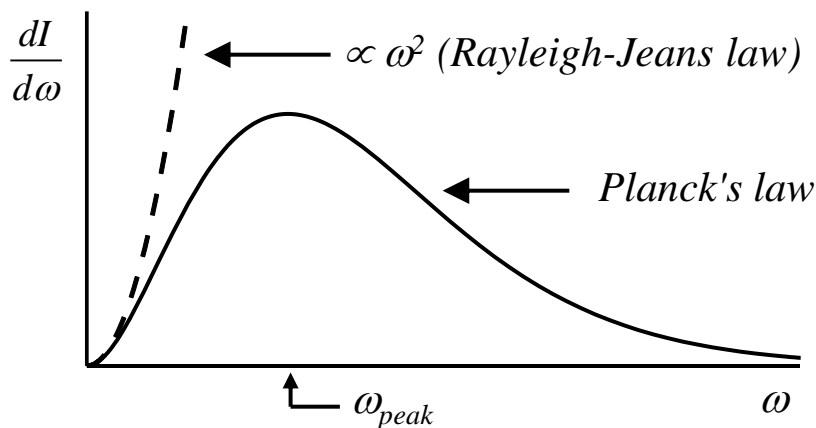
where  $du/d\omega$  is the *energy density per unit range of  $\omega$*  of the photons and  $c$  is their speed. (All photons have the same speed, of course).

A *black body* absorbs all radiant energy incident upon it. In thermal eq<sup>m</sup>, the black body must radiate the same amount of energy per unit time per unit area (or else it will gain or lose energy and so not be in eq<sup>m</sup>).

Hence the intensity (power per unit area) radiated per unit range of  $\omega$  by a black body in eq<sup>m</sup> at temperature  $T$  is

$$\frac{1}{4} \frac{du}{d\omega} c \equiv \boxed{\frac{dI}{d\omega} = \frac{\hbar \omega^3}{4\pi^2 c^2 \left[ e^{\hbar\omega/k_B T} - 1 \right]}} \quad \text{Planck's radiation law}$$

The classical *Rayleigh-Jeans law* of radiation can be obtained from Planck's law by setting  $\hbar = 0$ , and predicts  $dI/d\omega \propto \omega^2$ . This is the so-called *ultraviolet catastrophe*: the intensity rises without limit at high frequencies, and the total radiated intensity (integrated over all  $\omega$ ) is infinite!



Planck's law avoids this unphysical outcome because  $dI/d\omega$  turns over around  $\hbar\omega \sim k_B T$  and decreases for higher  $\omega$ .

This was how quantum theory got started - and where Planck's constant  $h$  (or  $\hbar$ ) was first introduced.

The frequency  $\omega_{peak}$  where the curve  $dI/d\omega$  is a maximum can be found by setting the derivative equal to zero:

$$\frac{d}{d\omega} \left( \frac{dI}{d\omega} \right) = 0 \quad [\text{problem sheet 3 Q 9}]$$

$$\Rightarrow \boxed{\omega_{peak} \propto T} \quad \underline{\text{Wien's displacement law}}$$

The frequency of maximum radiated intensity is proportional to  $T$ . That's why white-hot iron is hotter than red-hot iron, and blue stars are hotter than red stars. It's the basis of "colour temperature" in photography, and pyrometry for temperature measurement. The black-body "cosmic background" radiation from shortly after the Big Bang has cooled so much as the Universe expanded that it now peaks at microwave frequencies  $\omega_{peak}/2\pi = 160 \text{ GHz}$ , which is characteristic of  $T = 2.7 \text{ K}$ .

The constant of proportionality implicit in the last sentence is  $(k_B/\hbar) \times$  a dimensionless number that can be found numerically.

The total intensity radiated over all frequencies can be found by integrating  $dI/d\omega$ :

$$I_{total} = \int_0^\infty \left( \frac{dI}{d\omega} \right) d\omega \quad [\text{problem sheet 3 Q 10}]$$

$$\Rightarrow \boxed{I_{total} = \frac{\pi^2 k_B^4}{60 c^2 \hbar^3} T^4 \equiv \sigma T^4} \quad \underline{\text{Stefan's law}}$$

Hot stars lose energy (and die) much faster than cool stars.

## Appendix A: Binomial statistics

### A1. The factorial function

$$n! \equiv n \times (n-1) \times (n-2) \times \dots \times 3 \times 2 \times 1$$

Clearly it obeys the recurrence relation

$$n! = n \times (n-1)!$$

Substituting  $n = 1$  gives the result that  $0! = 1$ .

### A2. Sub-systems $SS_1$ and $SS_2$ have $N_1$ and $N_2$ accessible microstates respectively. How many accessible microstates does the combined system have?

For each state of  $SS_1$  there are  $N_2$  states of  $SS_2$ . Since there are  $N_1$  states of  $SS_1$ , the total number of states is  $N_1 \times N_2$ . This result generalises for more than two sub-systems: statistical weights multiply. (Implicit assumption: that the state of  $SS_1$  is independent of the state of  $SS_2$ .)

### A3. How many ways are there to order $N$ distinguishable objects in a list?

There are  $N$  options for 1st place in the list, with  $N - 1$  objects left unplaced.

$N - 1$  remaining options for 2nd place, with  $N - 2$  objects left unplaced.

$N - 2$  remaining options for 3rd place, with  $N - 3$  objects left unplaced.

...

2 remaining options for  $(N - 1)$ th place, with 1 object left unplaced.

1 remaining option for  $N$ th place, with no objects left unplaced.

So the total number of ways of ordering the objects is [see previous section]

$$N \times (N - 1) \times (N - 2) \times \dots \times 2 \times 1 = N!$$

Conclusion: there are  $N!$  times as many (ordered) sets of  $N$  distinguishable objects as there are (unordered) sets of  $N$  indistinguishable objects.

**A4. How many ways are there to divide  $N$  distinguishable objects between two sets, with  $n$  objects in the first set and  $N - n$  objects in the second set?**

Let the answer to the question be  $M$ .

For each way of dividing the objects, there are  $n!$  ways of ordering the  $n$  objects within the first set, and  $(N - n)!$  ways of ordering the  $N - n$  objects within the second set. [see previous section]

Since there are  $M$  ways of dividing the objects, the total number of ways of ordering the  $N$  objects is  $M \times n! \times (N - n)!$

But the total number of ways of ordering  $N$  distinguishable objects is  $N!$

Hence  $M \times n! \times (N - n)! = N!$  and

$$M = \frac{N!}{n!(N - n)!}$$

**A5. How many ways are there to divide  $N$  distinguishable objects between  $p$  sets, so that there are  $n_1$  objects in the first set,  $n_2$  objects in the second set, ...  $n_i$  objects in the  $i$ -th set?**

(Obviously we must have  $\sum n_i = N$  so that every object gets put in exactly one set.)

This is just the generalisation of the previous question. For each way of dividing the objects, there are  $n_i!$  ways of ordering the  $n_i$  objects within the  $i$ -th set, etc. Following the same argument, we get

$$M = \frac{N!}{r_1! r_2! \dots r_i! \dots r_p!}$$



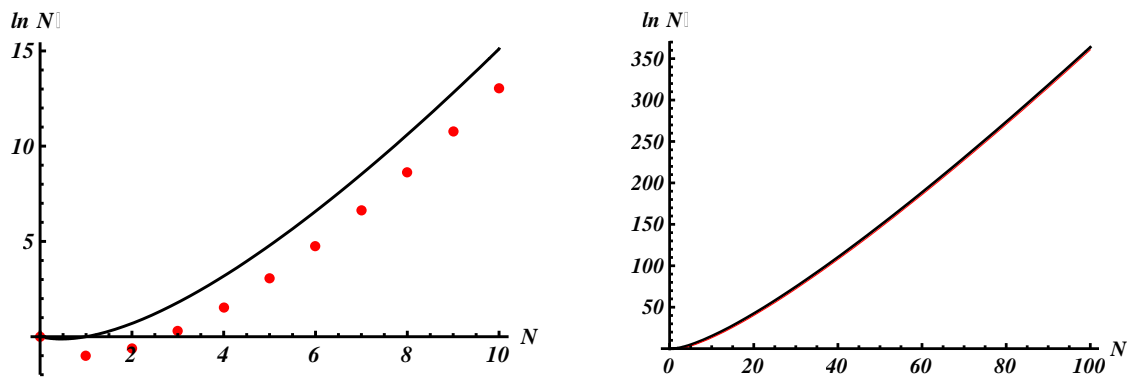
A6. Stirling's approximation for large factorials

The factorial of a large number is (a) very very large (for example,  $100! \approx 10^{158}$ , and 100 is a lot less than  $N_A$ ) and (b) not a function we know how to differentiate. Fortunately, in statistical mechanics we can manage these problems because we're usually interested in  $\ln(N!)$  rather than  $N!$ , which is a much more manageable number. For example,  $\ln(100!) \approx 364$  and  $\ln(N_A) \approx 3 \times 10^{25}$ .

There's an excellent approximation for  $\ln(N!)$  that gets more accurate as  $N$  gets bigger:

$$\ln(N!) \approx N \ln N - N \qquad \text{(Stirling's formula for large } N)$$

Here are two plots of the exact value of  $\ln(N!)$ , together with Stirling's approximation for it. The red data are the exact values, while the black curves are the approximation. On the right hand graph you can see that the approximation is indistinguishable from the exact values for large  $N$ .



The approximate form is straightforward to differentiate, for example when finding thermodynamic variables from statistical weights.

## Appendix B: Particle in a box

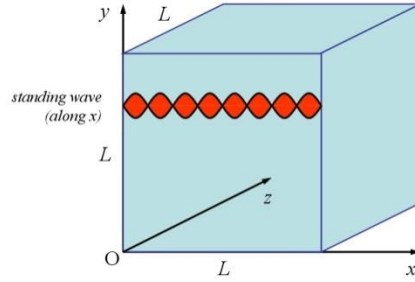
To analyse quantum gases, we need to know about the quantum states of a single particle in a box. The particles can be gas molecules, atoms, elementary particles eg electrons or neutrons, or photons. (The results do not need to be memorised.)

### B1. Allowed wavevectors

It is a result of quantum theory (de Broglie's equation) that a particle of momentum  $\mathbf{p}$  can behave as a wave with wavevector  $\mathbf{k}$  such that

$$\mathbf{p} = \hbar \mathbf{k} \quad (1)$$

We therefore need to know the values of  $\mathbf{k}$  that are allowed for any wave inside a box. For simplicity we assume the box is cubic with length of side  $L$  and volume  $V = L^3$ , with opposite corners at  $(0, 0, 0)$  and  $(L, L, L)$ , and the wave function  $\psi = 0$  at the walls. (These assumptions do not change the final result but do make it easier to derive.)



The wave function for a quantum state must therefore be a standing wave

$$\psi(x, y, z) = \sin(k_x x) \sin(k_y y) \sin(k_z z) \quad (2)$$

(so that  $\psi = 0$  at the walls where each co-ordinate = 0) with each wavevector component

$$k_x = \frac{\pi}{L} n_x \quad k_y = \frac{\pi}{L} n_y \quad k_z = \frac{\pi}{L} n_z \quad (3)$$

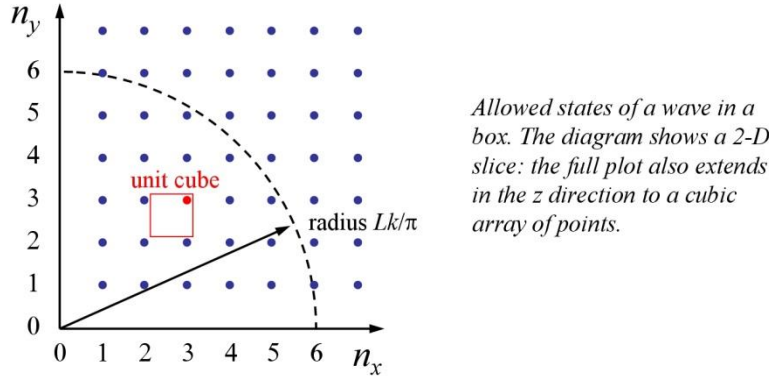
where each "quantum number"  $n_x, n_y, n_z$  is a positive integer 1, 2, 3, ... (so that  $\psi = 0$  at the walls where each co-ordinate =  $L$ ). Hence the allowed wave constants  $k$  (magnitudes of the wavevector  $\mathbf{k}$ ) are

$$\begin{aligned} k = |\mathbf{k}| &= (k_x^2 + k_y^2 + k_z^2)^{1/2} \\ &= \frac{\pi}{L} (n_x^2 + n_y^2 + n_z^2)^{1/2} \end{aligned} \quad (4)$$

with a single state for each ordered set of natural numbers  $n_x, n_y, n_z$ .

### B2. Number of states with wave constant $\leq k$

In an abstract space with co-ordinate axes  $n_x, n_y, n_z$ , each allowed state is represented by a point with positive integer co-ordinates. Note that eq. (4) is the equation of a sphere in this space with radius  $Lk/\pi$ . Thus the total number  $G(k)$  of states with wave constant  $\leq k$  is the number of points within the 1/8 of the sphere that has all-positive co-ordinates. If we consider that each state "owns" the unit cube whose outer corner is the point that represents the state, then  $G(k)$  is approximately the volume of 1/8 of a sphere of radius  $Lk/\pi$ . This is a very good approximation when  $k$  is large because only a small proportion of the states being counted lie near the surface of the sphere, which is where any discrepancies arise.



From the formula for the volume of a sphere:

$$G(k) = \frac{1}{8} \times \frac{4}{3} \pi \left( \frac{Lk}{\pi} \right)^3 = \frac{Vk^3}{6\pi^2} \quad (5)$$

We assumed that each  $n_x, n_y, n_z$  corresponds to one state. But if the particle has internal degrees of freedom (eg spin) so that each point corresponds to  $g_I$  states, then

$$G(k) = \frac{g_I Vk^3}{6\pi^2} \quad (6)$$

### B3. Density of states in terms of $k$

The derivative of eq. (6)

$$\frac{dG}{dk} = \frac{g_I Vk^2}{2\pi^2} \quad (7)$$

is called the density of states per unit  $k$ , such that  $(dG/dk)\delta k$  is the number of states with wave constant between  $k$  and  $k + \delta k$  (see main text).

**B4. Density of states in terms of  $E$** 

The density of states per unit  $E$  (or any other variable) can be found by the chain rule

$$\frac{dG}{dE} = \frac{dG}{dk} \frac{dk}{dE} \quad (8)$$

Eq. (7) for  $dG/dk$  is universal for any wave in a box. But the conversion to  $dG/dE$  (or to a related quantity such as photon frequency) depends on its "dispersion relation"  $k(E)$ , which in turn depends on what kind of particle it is.

**B4.1. Ordinary non-relativistic (massive) particles**

First relate  $E$  and  $k$  using the kinetic energy formula

$$\begin{aligned} E &= \frac{1}{2}mv^2 \quad (\text{mass } m, \text{ speed } v, \text{ non-relativistic}) \\ &= \frac{p^2}{2m} \quad (\text{magnitude of momentum } p = mv) \\ &= \frac{\hbar^2 k^2}{2m} \quad (\text{de Broglie } p = \hbar k) \end{aligned} \quad (9)$$

$$k(E) = \frac{(2mE)^{1/2}}{\hbar} \quad (10)$$

$$\Rightarrow \frac{dk}{dE} = \frac{1}{\hbar} \left( \frac{m}{2E} \right)^{1/2} \quad (11)$$

Substitute eqs. (7) and (11) into eq. (8) and use eq. (10) to eliminate  $k$ , giving

$$\boxed{\frac{dG}{dE} = \frac{g_I}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} V E^{1/2}} \quad (12)$$

The degeneracy  $g_I$  will depend on further details of the nature of the particle, eg its spin.

**B4.2. Photons (and other "ultra-relativistic" particles)**

As before, relate  $E$  and  $k$  using what you know about the physics of the particle. In this case, photon energy

$$E = \hbar\omega = \hbar ck \quad (13)$$

$$k(E) = \frac{E}{\hbar c}$$

$$\frac{dk}{dE} = \frac{1}{\hbar c}$$

$$\begin{aligned} \frac{dG}{dE} &= \frac{dG}{dk} \frac{dk}{dE} \\ &= \frac{g_I V}{2\pi^2} \times \frac{E^2}{\hbar^2 c^2} \times \frac{1}{\hbar c} \end{aligned}$$

Photons can exist in two independent states of polarisation, so  $g_I = 2$ :

$$\frac{dG}{dE} = \frac{VE^2}{\pi^2 \hbar^3 c^3} \quad (14)$$

More useful is the density of states per unit  $\omega$ , using eq. (13):

$$\begin{aligned} \frac{dG}{d\omega} &= \frac{dG}{dE} \times \frac{dE}{d\omega} \\ &= \frac{V \hbar^2 \omega^2}{\pi^2 \hbar^3 c^3} \times \hbar \end{aligned}$$

$$\boxed{\frac{dG}{d\omega} = \frac{V \omega^2}{\pi^2 c^3}} \quad (15)$$

**B5. Energy of a particle in a box**

Substitute eq. (4) for the allowed wave constants into the appropriate dispersion relation  $E(k)$ . For non-relativistic particles, that's eq. (10):

$$E = \frac{\pi^2 \hbar^2}{2mV^{2/3}} (n_x^2 + n_y^2 + n_z^2) \quad (16)$$

and for photons use  $\omega = ck$ :

$$\omega = \frac{\pi c}{V^{1/3}} (n_x^2 + n_y^2 + n_z^2)^{1/2} \quad (17)$$

**Appendix C: Integrals of gaussian functions**

It can be shown that, for  $a$  positive

$$I_n = \int_0^\infty x^n e^{-ax^2} dx = \frac{1}{2a^{(n+1)/2}} \left( \frac{n-1}{2} \right)!$$

where (for avoidance of doubt) the factorial function acts on  $(n-1)/2$ . This is straightforward when  $n$  is an odd number, but when  $n$  is even we need the factorial of a fraction. To handle this, take (as given) the following value for the factorial of minus one half:

$$\left( -\frac{1}{2} \right)! = \sqrt{\pi}$$

which can be derived from the integral with  $n = 0$ , and use the familiar recurrence relation

$$N! = N \times (N-1)!$$

for higher values. For example,

$$\left( \frac{3}{2} \right)! = \frac{3}{2} \times \frac{1}{2} \times \left( -\frac{1}{2} \right)! = \frac{3\sqrt{\pi}}{4}$$

Although fractional factorials are unfamiliar, the formula works well.

Appendix D: Geometric progression

D1. Sum of  $e^{-am}$

$$\sum_{m=0}^{\infty} e^{-am} = \frac{1}{1 - e^{-a}}$$

This is just a geometric progression. See the second result on p. 6 of the formula book, with  $r = e^{-a}$  and  $n \rightarrow \infty$ .

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$$a = (a + d) + (a + 2d) + \cdots + (a + |n - 1|d)$$
$$\longrightarrow 1 + r + r^2 + \cdots + r^n$$
$$1 + 2 + 3 + \cdots + n$$

$$= \frac{n}{2}(2a + |n - 1|d)$$
$$= \frac{1 - r^{n+1}}{1 - r}$$
$$= \frac{1}{2}n(n + 1)$$

D2. Sum of  $me^{-am}$

Take minus the previous result and differentiate with respect to  $a$ :

$$\begin{aligned} \frac{d}{da} \left[ - \sum_{m=0}^{\infty} e^{-am} \right] &= \frac{d}{da} \left[ \frac{-1}{1 - e^{-a}} \right] \\ \Rightarrow \sum_{m=0}^{\infty} me^{-am} &= \frac{e^{-a}}{(1 - e^{-a})^2} \end{aligned}$$