

The physical model of **heat**, *thermodynamics*, is in essence a theory of the statistical average motion of a large number of *microscopic* particles which constitute the *macroscopic* entity (e.g. a litre of liquid water) being studied.

The basic idea is that **temperature** is proportional to the **mean kinetic energy of molecules**, and **heat** is the **total amount of energy transferred** (e.g. to your hand when you insert it into a warm bath). Temperature is therefore a *microscopic* concept (e.g. an average quantity of molecules) whereas heat is a *macroscopic* quantity.

**Kinetic Theory** is essentially a *statistical* theory of the motion of molecules. It can be used to *explain bulk properties of matter* since the sizes of molecules (or atoms) are *very* small compared to human-sized macroscopic objects like vials of liquid or bottles of gas. In other words, the number of molecules and interactions in most practical scenarios is a *huge* number. In Kinetic Theory, we consider *average* physical quantities such as speed, pressure, heat flux etc, since the huge number of molecules makes a mechanical calculation impractical. Inspired by the observation of **Brownian motion**, we shall assume molecular motion is a *random* process. This assumption of randomness will enable us to *calculate* average physical quantities based upon knowledge of their *probability distributions*.

Note a cubic metre of densely packed atoms will have about  $1/(10^{-10})^3 = 10^{30}$  atoms, since the size of an atom is about  $10^{-10}$  m. Indeed a mole of a chemical substance (e.g. about 18 grams of water) is defined to have **Avogadro's number** of molecules  $N_A = 6.02 \times 10^{23}$ .

**Random walk and mean free path.** If the average molecular speed is  $\langle v \rangle$ , which might be the RMS speed  $\sqrt{\langle v^2 \rangle}$ , the RMS distance travelled in  $t$  seconds is:  $\sqrt{\langle x^2 \rangle} = l\sqrt{N} = \sqrt{l\langle v \rangle t}$  where  $N$  is the number of collisions between

molecules, and the mean free path  $l$  is the average distance between collisions.  $l = \frac{1}{\pi\sqrt{2}d^2n}$  where  $d$  is the molecular diameter and  $n$  is the number of molecules per unit volume. For an ideal gas:  $l = \frac{k_B T}{\pi\sqrt{2}d^2 p}$  since the number of moles is

$\frac{nV}{N_A}$  and hence:  $pV = \frac{nV}{N_A} RT \therefore n = \frac{p}{k_B T}$ . *Knudsen's number* (Kn) is the ratio  $Kn = l/d$ . i.e. the mean free path in terms of molecular diameters. If Kn is *large* this implies *statistical mechanics is the most appropriate model of molecular motion*. If Kn is much closer to unity, then *continuum fluid mechanics* is required. i.e. distinct particles making random collisions where we can ignore molecular sizes is *not* appropriate.

By considering elastic collisions of molecules with the walls of a container, the pressure  $p$  of a gas of density  $\rho$  is

$p = \frac{1}{3}\rho\overline{v^2}$  where  $\overline{v^2}$  is the mean-squared molecular speed.

**Boltzmann factor.** If a large number of particles are exchanging energy in a random manner, the probability that a particle will have energy between  $\varepsilon$  and  $\varepsilon + d\varepsilon$  is proportional to  $e^{-\frac{\varepsilon}{k_B T}}$  where  $T$  is the absolute temperature (in K) and  $k_B$  is Boltzmann's constant  $k_B = 1.381 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$ .

This leads to the *Maxwell-Boltzmann distribution* of energies, and molecular speeds, if all energy is kinetic

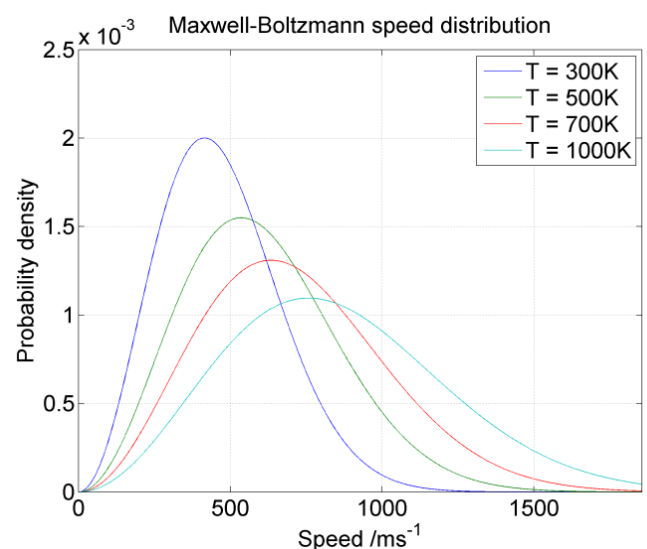
$\varepsilon = \frac{1}{2}mv^2$ .  $m$  is the molecular mass. Motion is assumed to be  $x, y, z$  (3D) translation only.

$$p(\varepsilon)d\varepsilon = \frac{2}{\sqrt{\pi}} \left( \frac{1}{k_B T} \right)^{\frac{3}{2}} \sqrt{\varepsilon} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

$$p(v)dv = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2}mv^2/k_B T} dv$$

The mean energy is:  $E\left[\frac{1}{2}mv^2\right] = \frac{3}{2}k_B T$  i.e.  $\frac{1}{2}k_B T$  for every degree of freedom of molecular motion. This is the

'*theory of equi-partition*'. Note also:  $v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}}$ .



**NOTE:**  $k_B = R/N_A$

## Entropy

In Classical Thermodynamics, Rudolf Clausius proposed the *Second Law*, which is most simply stated as “for any physical process, the total entropy of the Universe must increase.” The change in entropy  $S$  is defined as the ratio of the *reversible*

heat change to the absolute temperature.  $dS = \frac{dQ}{T}$ .

Ludwig Boltzmann and Josiah Gibbs proposed a *statistical* basis for entropy. The most general form is the Gibbs definition:

$S = -k_B \sum_i p_i \ln p_i$  where  $p_i$  is the probability of each *microstate* of a given system.

If all microstates (i.e. the energy configuration of all the constituent molecules) are equally probable,  $S = k_B \ln W$  where  $W$  is the number of distinct microstates, or “the number of ways of arranging energy in a system.”

## Question 1

- (i) Calculate the mean free path of a ideal gas molecule of diameter 0.3nm at sea-level, where pressure is 1atm = 101,325Pa and temperature is 20°C. Calculate the *Knudsen number*. Is a *statistical* approach to analyzing the motion of the gas molecule valid?
- (ii) Use the *equipartition* result  $\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T$  to work out the RMS speed (in m/s) of an oxygen (O<sub>2</sub>) molecule, which comprises about 21% of the air we breathe (by volume). As in (i), let the temperature be 20°C. The mass of an oxygen molecule is:  $m = 15.999 \times 1.661 \times 10^{-27}$  kg .
- (iii) If the RMS distance travelled by a molecule in time  $t$  is  $\sqrt{\langle x^2 \rangle} = l\sqrt{N} = \sqrt{l\langle v \rangle}t$ , combine the results in (i) and (ii) and sketch a graph of how far an oxygen molecule may travel between 0 and 60s.
- (iv) Two colourless gases X and Y, whose molar masses are in the ratio 17 : 36.5 are released from opposite ends of a 1.00m tube. They diffuse along the tube until they meet. At this point they react and produce an opaque cloud. If the temperature of the system is constant, calculate the distance from the X end of the tube where this cloud occurs.

What would happen to the position of the cloud of molecule Y was  $M = 3$  times more massive? Suggest molecules for the gases X,Y.

- (v) A gas consisting of molecules of diameter 0.4nm is contained in a sealed syringe. The initial pressure is 1atm = 101,325Pa and the temperature is 18°C. If the gas is compressed slowly such that temperature does not change, at what pressure (in atm) does the mean free path equal the molecular diameter? Comment on the state of matter of the molecules at this point.
- (vi) By considering elastic collisions in  $x,y,z$  directions of  $N$  gas molecules of mass  $m$  trapped in a cubical box of side length  $a$ , show that if motion is random, the average pressure exerted on the walls of the cube is  $p = \frac{1}{3}\rho\overline{v^2}$  where  $\overline{v^2}$  is the mean-squared molecular speed and  $\rho$  is the density of the gas. If the density of air is 1.23kg/m<sup>3</sup>, calculate the RMS speed of air molecules if air pressure is 101,325Pa.
- (vii) The time  $t$  for a chemical reaction to complete varies with temperature according to a *Boltzmann factor*.  
 $\frac{1}{t} = Ae^{-\frac{\epsilon}{RT}}$  where  $\epsilon$  is the ‘Activation energy’,  $T$  is the absolute temperature,  $R = 8.314\text{Jmol}^{-1}\text{K}^{-1}$  and  $A$  is a constant. If  $t = 30.0\text{s}$  at  $T = 300\text{K}$  and  $t = 7.0\text{s}$  at  $T = 340\text{K}$ , calculate  $\epsilon$  and  $A$ .
- (viii) Prove the following results using the *Maxwell-Boltzmann* molecular speed distribution:

$\int_0^\infty p(v)dv = 1$ ,  $E[\frac{1}{2}mv^2] = \frac{1}{2}m\int_0^\infty v^2 p(v)dv = \frac{3}{2}k_B T$ . Use the standard integrals:

$$I_n = \int_0^\infty x^n e^{-ax^2} dx; \quad I_n = \frac{n-1}{2a} I_{n-2}; \quad I_0 = \frac{1}{2}\sqrt{\frac{\pi}{a}}; \quad I_1 = \frac{1}{2a}; \quad I_2 = \frac{\sqrt{\pi}}{4a^{\frac{3}{2}}}.$$

## Question 2

The boiling point of water  $T_{boil}$  varies with atmospheric pressure  $p$  using an

equation that contains a Boltzmann factor:  $p = p_0 e^{\frac{L_{vap}}{R} \left( \frac{1}{T_0} - \frac{1}{T_{boil}} \right)}$  where

$p_0 = 101,325 \text{ Pa}$  and  $T_0 = 373 \text{ K}$ , i.e. the boiling point of water at a pressure of one atmosphere. The molar gas constant is  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

By plotting a suitably linearized graph, use the following data to calculate the latent heat of vaporization of water in kJ/mol. Compare your answer to the official value of  $L_{vap} = 43.8 \text{ kJ mol}^{-1}$ .

Tboil /degC	Tboil /K	pressure p /kPa
40.7	313.7	6.5
45.4	318.4	9.1
49.5	322.5	13.9
55.9	328.9	15.7
59.6	332.6	17.8
64.5	337.5	23.4
65.9	338.9	28.1
69.9	342.9	30.6
71.6	344.6	34.6
77.8	350.8	42
81.0	354	47.9
84.9	357.9	56.5
88.6	361.6	63.8
90.5	363.5	68.5
93.2	366.2	75.2

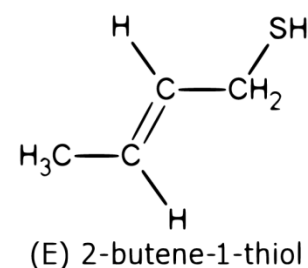
## Question 3

(i) Skunk spray is composed of three *thiol* compounds, one of which is (E)-2-butene-1-thiol

which has a molecular weight of 88.2g/mol. A skunk releases this chemical  $x = 10.0 \text{ m}$

from a tourist. Assume the molecular weight of air is 29g/mol

- The temperature is  $28^\circ \text{C}$ , and pressure is  $p = 10^5 \text{ Pa}$
- The skunk musk and air are in thermal equilibrium, and the thiol molecule reaches the tourist's nose via diffusion
- The internal energy of one mol of gas is  $\frac{3}{2} RT$  where  $R = 8.314 \text{ J mol}^{-1} \text{ K}$



Calculate the RMS speed  $v$  of air molecules, then find the RMS speed of the thiol molecule. How long will it take /s for the spray to reach the nose of the tourist? Does it seem a bit quick?

(ii) The *diffusion distance* of the thiol molecules is  $x \approx \sqrt{lvt}$  where the *mean free path*  $l = \frac{k_B T}{\pi \sqrt{2} d^2 p}$ . What is the

emission-to-sniff time  $t$  now? Take a sensible molecular size  $d = 0.5 \text{ nm}$ .

Note if you use these equations *you will get a very strange result!* Do *all* the skunk musk molecules have to undergo a random walk from the skunk to the tourist, for the tourist to smell the skunk?

## Question 4

(i) Show that the pressure change in a column of ideal gas of density  $\rho$  as one gains  $dh$  in altitude is:

$$dP = -\rho g dh$$

(ii) If the atmosphere is isothermal, i.e. at constant temperature  $T$ , and comprised of ideal gas, show that:

$$P = P_0 e^{-\frac{mgh}{k_B T}}$$

where  $m$  is the mass of a gas molecule and  $P_0$  is the atmospheric pressure at  $h = 0$ .

Sketch the variation with pressure with height, and calculate the altitude in m which corresponds to a 50% reduction in atmospheric pressure. Assume  $T = 10^\circ \text{C}$ .

### Question 5

Boltzmann's definition of *Entropy* states:  $S = k_B \ln W$  where  $W$  is the *number of ways or ways of arranging energy in a system*. Consider a simple system of  $N$  containers and  $M$  quanta of energy (each of energy  $\varepsilon$ ). Using lines  $|$  to represent the boundaries of the containers and  $x$  to represent the energy quanta, a  $N = 3, M = 2$  system could have the following states:

#1  $|xx| | |$ , #2  $| |xx| |$ , #3  $| | |xx|$ , #4  $|x|x| |$ , #5  $| |x|x|$ , #6  $|x| |x|$

i.e. *six* ways. Since  $N$  containers mean  $N + 1$  vertical lines  $|$ , and two  $|$  must always represent the boundaries, the number of ways of arranging  $M \times \varepsilon$  in  $N$  containers is:

$$W = \frac{(N + 1 - 2 + M)!}{M!(N + 1 - 2)!} = \frac{(N + M - 1)!}{M!(N - 1)!}$$

So when  $N = 3, M = 2$ ,  $W = \frac{(N + M - 1)!}{M!(N - 1)!} = \frac{(3 + 2 - 1)!}{2!(3 - 1)!} = \frac{4!}{2!2!} = \frac{4 \times 3}{2} = 6$ .

A system of ten energy quanta shared among five atoms is mixed with a system of five quanta shared among ten atoms. If all atoms are identical, calculate the entropy change  $\Delta S$  in units of  $k_B$  following the mixing of the systems.

### Question 6

The probability of a beam of molecules travelling through an identical molecular medium surviving distance between  $x$  and

$x + dx$  is given by:  $p(x)dx = \frac{e^{-\frac{x}{l}}}{l} dx$ , where  $l$  is the mean free path. This is called the *Beer-Lambert Law*.

- (i) Sketch  $p(x)$  vs  $x$ .
- (ii) Show that  $\int_0^\infty p(x)dx = 1$  and  $E[x] = \int_0^\infty xp(x)dx = l$ .
- (iii) Calculate the probability that  $x \geq l$ .

### Question 7

A system consists of randomly interacting particles that can either be of zero energy, or energy  $\varepsilon$ .

The *Boltzmann Factor* concept states that the probability of a particle in the system having energy  $E$  is:

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

(i) Show that  $A = \frac{1}{1 + e^{-\varepsilon/k_B T}}$

(ii) Show that the mean energy per particle is:  $\bar{E} = \frac{\varepsilon}{e^{\varepsilon/k_B T} + 1}$

(iii) Sketch  $\bar{E}$  vs  $T$  and comment on the result. *Hint:* What happens when  $T$  is very large, or very small?

(iv) In Einstein's model of a solid, the solid is assumed to vibrate at a fixed frequency  $f$ . Borrowing an idea from Black Body radiation (see the QM course!)

$$\bar{E} = \frac{hf}{e^{hf/k_B T} - 1}$$

Planck's constant  $h = 6.63 \times 10^{-34}$  Js

(a) Sketch  $\bar{E}$  vs  $T$ . You will probably want to first evaluate  $\frac{d\bar{E}}{dT}$  and work out what this tends to as  $T \rightarrow 0$  and  $T \rightarrow \infty$ .

(b) The molar heat capacity is given by  $C = 3N_A \frac{d\bar{E}}{dT}$ . If not already done so, evaluate this using calculus and sketch  $C$  vs  $T$ . Show that as  $T$  becomes large, the molar heat capacity tends to a fixed value of  $3R$ .

*Hints:*

You need to prove that:

$$x = \frac{hf}{k_B T}$$
$$C = 3R \frac{x^2 e^x}{(e^x - 1)^2}$$