Physics Enrichment Program HKUST
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Written by Tony Shing

- Pre-requisite : Probability on Continuous Variable
- Boltzmann Factor
- Derivation of Maxwell - Boltzmann Distribution

Some basics about statistics

First you need to know how probability is described for random number when the number is from a continuous interval

Probability Mass Function (PMF)

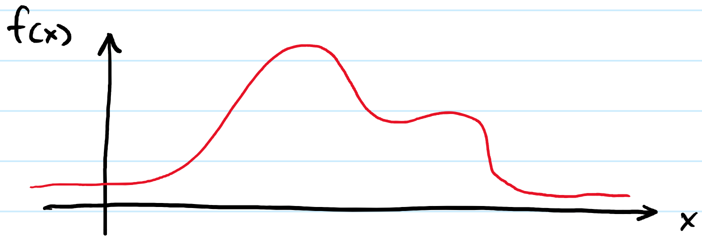
For random variables that can be picked from a finite number of cases, we describe them by Probability Mass Function (or simply called probability)

E.g. Throw 2 dices & sum their values

$\Rightarrow$ A list of different probabilities to get 2 to 12

Probability Density Function (PDF)

For random variables that can appear as any value within an interval, we describe them by Probability Density Function



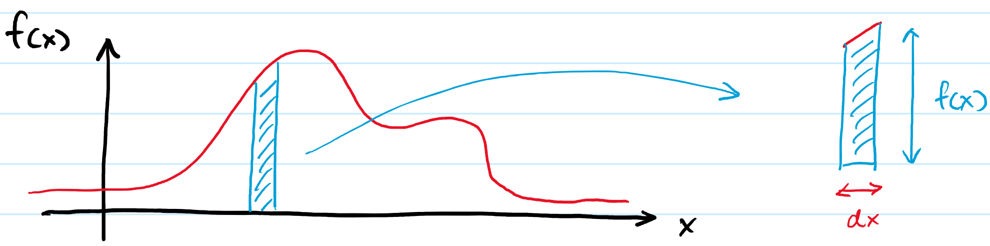
☆ PDF is not describing the probability of getting a particular value

∵ There are infinitely many real no. in the interval

⇒ Probability of getting an exact value = 0

☆ PDF is used for describing the probability of getting a value within an interval $[x_0, x_0 + dx]$

i.e. $\underbrace{P(x_0 < x < x_0 + dx)}_{\text{prob. of inside the interval}} = \underbrace{f(x)}_{\text{height}}\underbrace{dx}_{\text{width}}$



⇒ Probability is represented by area under curve

NOT the curve's height

⇒ This is why f(x) is called probability density

Normalization of Probability

Normalize = Sum up to 1   A requirement of probability

PMF ⇒ All prob. add up to 1

$$\sum_{\text{all } x} P(x) = 1$$

PDF ⇒ The whole area under curve = 1
i.e. by integration

$$\int_{-\infty}^{\infty} f(x)\,dx = 1$$

Expected Value

= The weighted average of all outcomes by probability

~ Average value you get after repeating ∞ times

PMF : $E(x) = \sum_{\text{all } x} x\,P(x)$

PDF : $E(x) = \int_{-\infty}^{\infty} x\,f(x)\,dx$

E.g. A very unfair dice with 90% getting "1", 2% for other value

⇒ Average value we get after tossing it many times :

$$E(x) = \sum_{x=1 \text{ to } 6} x\,P(x)$$

$$= 1 \times 0.9 + (2+3+4+5+6) \times 0.02$$

$$= 1.3$$

Boltzmann Probability Distribution

In previous tutorials, we have only dealt with close systems.

i.e. No energy exchange, constant total energy

Question: How will the distribution of multiplicity changes when energy is allowed to change?

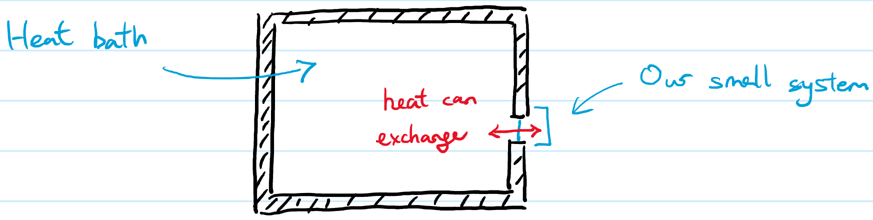
Imagine the system is thermally contacted to a hugh heat bath so there can be energy exchange

$\boxed{1}$ Heat bath is so big that all energy exchange has no effect on it

⇒ The heat bath's temperature ~ constant $= T_{bath}$

$\boxed{2}$ Heat bath is thermally isolated from everything except our system

⇒ Total energy $= U_{bath} + U_{sys} = \text{const.}$



We can think of the heat bath like the atmosphere

⇒ Large enough that any small system on Earth will not cause any significant change in its temperature

Our system & the heat bath may have different formula in the entropy - energy relation:

$$S_{bath} = S_{bath}(U_{bath}) \quad , \quad S_{sys} = S_{sys}(U_{sys})$$

① As a single system, the total entropy is a function of U_{sys}

$$S_{TOT} = S_{bath}(U_{bath}) + S_{sys}(U_{sys})$$

$$= S_{bath}(\underbrace{U_{TOT}}_{\text{Total energy = constant.}} - U_{sys}) + S_{sys}(U_{sys})$$

Then in terms of multiplicity

$$W_{TOT}(U_{sys}) = e^{\frac{S_{bath}(U_{TOT}-U_{sys})}{k}} \cdot e^{\frac{S_{sys}(U_{sys})}{k}}$$

② Taylor expanding $S_{bath}(U_{TOT}-U_{sys})$ by $U_{TOT} \gg U_{sys}$

$$S_{bath}(U_{TOT}-U_{sys}) \simeq S_{bath}(U_{TOT}) - \left.\frac{dS_{bath}}{dU}\right|_{U=U_{TOT}} \cdot U_{sys}$$

$$= S_{bath}(U_{TOT}) - \boxed{\frac{1}{T_{bath}}} \cdot U_{sys}$$

by $\frac{1}{T} = \frac{\partial S}{\partial U}$

$$\Rightarrow \underbrace{W_{TOT}(U_{sys})}_{\substack{\text{Total multiplicity of heat bath} \\ \text{+ system, when vary by} \\ \text{internal energy in the system}}} \simeq \underbrace{e^{\frac{S_{bath}(U_{TOT})}{k}}}_{\substack{\text{A constant} \\ \text{independent of } U_{sys}}} \cdot \underline{\underline{e^{\frac{-U_{sys}}{kT_{bath}}}}} \cdot \underbrace{e^{\frac{S_{sys}(U_{sys})}{k}}}_{\substack{\text{Multiplicity of the system} \\ \text{when it is alone}}}$$

New factor that depends on T_{bath}

$\Rightarrow$ Called <u>Boltzmann Factor</u>

$$= C \cdot e^{\frac{-U_{sys}}{kT_{bath}}} \cdot W_{sys}(U_{sys})$$

$\Rightarrow$ When our system is allowed to have heat exchange with a heat bath of temperature T_{bath}, $W \rightarrow W \cdot C e^{\frac{-U}{kT_{bath}}}$

③ Convert to probability by normalization

$$P\left(\begin{array}{c}\text{our system}\\ \text{having energy}\\ U_{sys}\end{array}\right) = \frac{W_{TOT}(U_{sys})}{\sum\limits_{\substack{\text{all possible}\\ \text{value of } U_{sys}}} W_{TOT}(U_{sys})} = \frac{e^{\frac{-U_{sys}}{kT_{bath}}} W_{sys}(U_{sys})}{\sum\limits_{\substack{\text{all possible}\\ \text{value of } U_{sys}}} e^{\frac{-U_{sys}}{kT_{bath}}} W_{sys}(U_{sys})}$$

Terminology :

- The denominator $\sum e^{\frac{-U}{kT}} W(U)$ is called "Partition Function"
- In the special case $W(U) = 1$, $P(U)$ is called "Boltzmann Distribution"

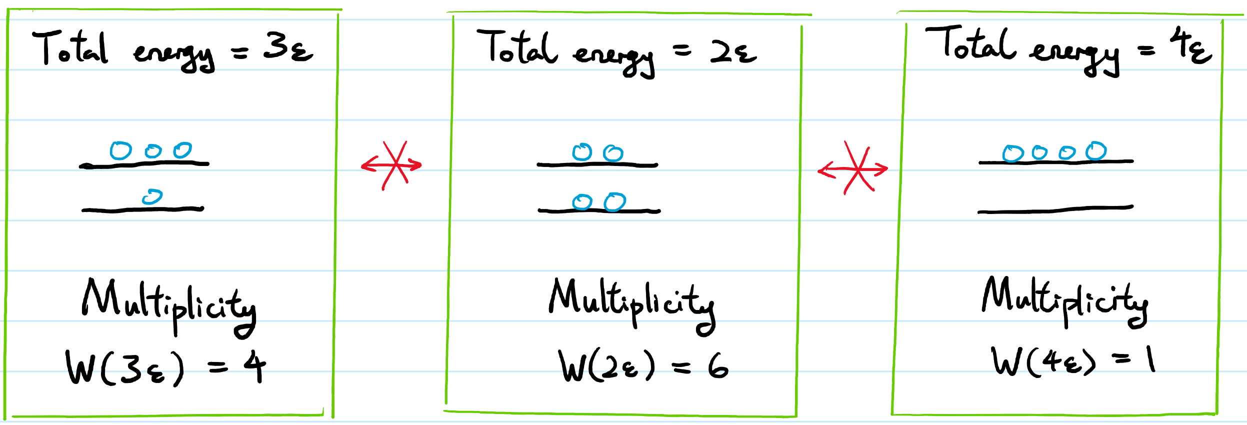
E.g. 2 boxes model, but balls in right box have higher energy

——— $E_R = \varepsilon$ ← Any ball in box R has energy ε

——— $E_L = 0$ ← Any ball in box L has energy 0

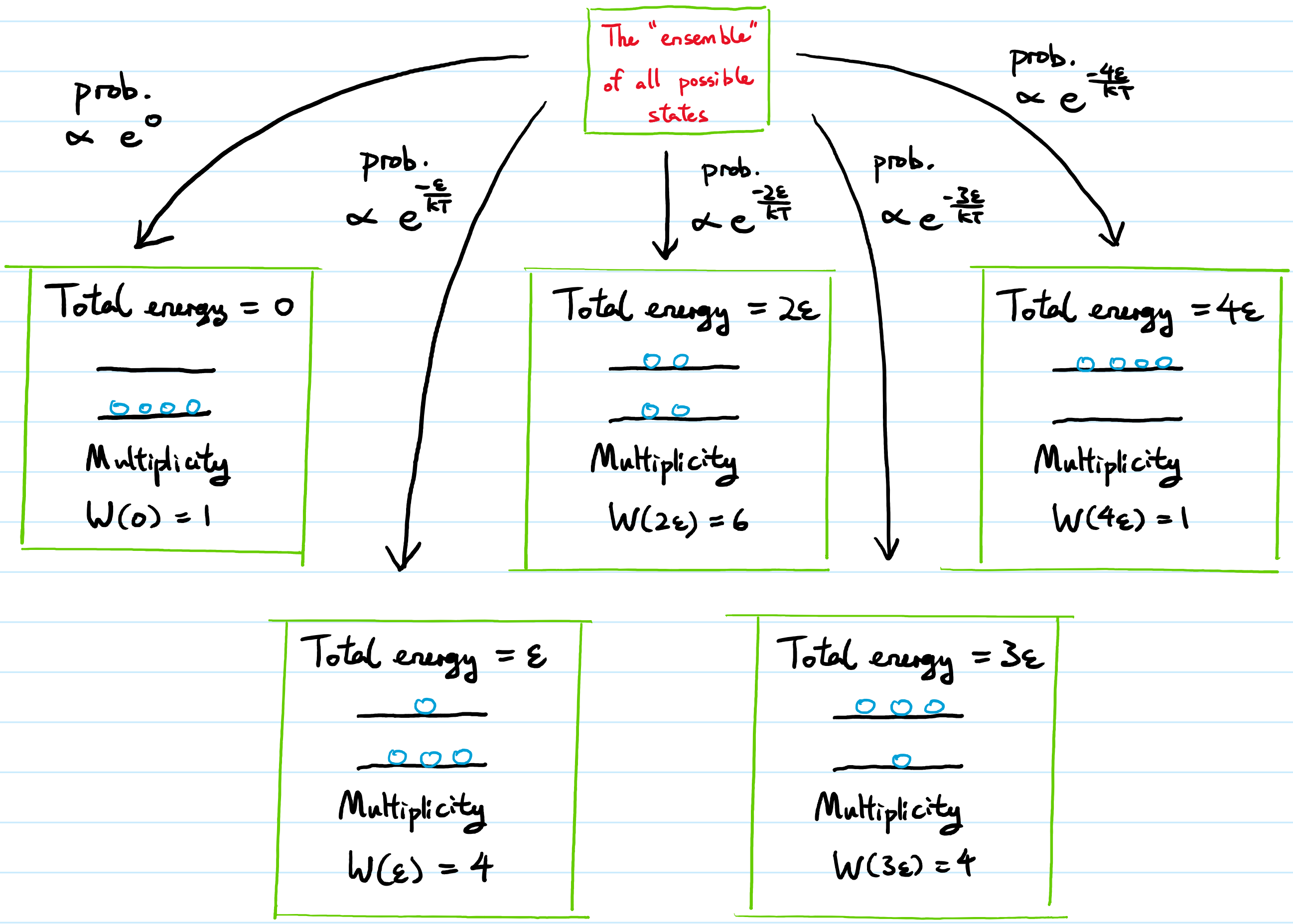
① When total energy is fixed

Cannot switch between states with different energy



② When heat can exchange with heat bath (temperature = T)

Can switch between states of different energy



To find the exact probability of each state, first need to calculate the partition function (Denominator)

$$Z = \sum_{\text{all energy } U} e^{-\frac{U}{kT}} W(U)$$

$$= e^{0} \times 1 + e^{-\frac{\varepsilon}{kT}} \times 4 + e^{-\frac{2\varepsilon}{kT}} \times 6 + e^{-\frac{3\varepsilon}{kT}} \times 4 + e^{-\frac{4\varepsilon}{kT}} \times 1$$

So the exact probabilities are

Energy :	0	ε	2ε	3ε	4ε
Prob :	$\frac{1}{Z}$	$\frac{4e^{-\frac{\varepsilon}{kT}}}{Z}$	$\frac{6e^{-\frac{2\varepsilon}{kT}}}{Z}$	$\frac{4e^{-\frac{3\varepsilon}{kT}}}{Z}$	$\frac{e^{-\frac{4\varepsilon}{kT}}}{Z}$

Maxwell - Boltzmann Distribution

The most important application of the above idea is finding the energy - probability relation for states in ideal gas when heat exchange is allowed.

Since energy of ideal gas can be any real number, We first need to convert the previous formula for continuous distribution

i.e. $$\sum_{\text{all possible } U} e^{-\frac{U}{kT}} W(U) \longrightarrow \int_0^{\infty} e^{-\frac{U}{kT}} W(U)\, dU$$

the prob. of having energy between $[U, U+dU]$

What is $W(U)$ for ideal gas ?

① Energy of ideal gas particle = its KE

$$U = \frac{1}{2} m |\vec{v}|^2 = \frac{1}{2} m \left(v_x^2 + v_y^2 + v_z^2 \right)$$

which depends on the velocity's magnitude only

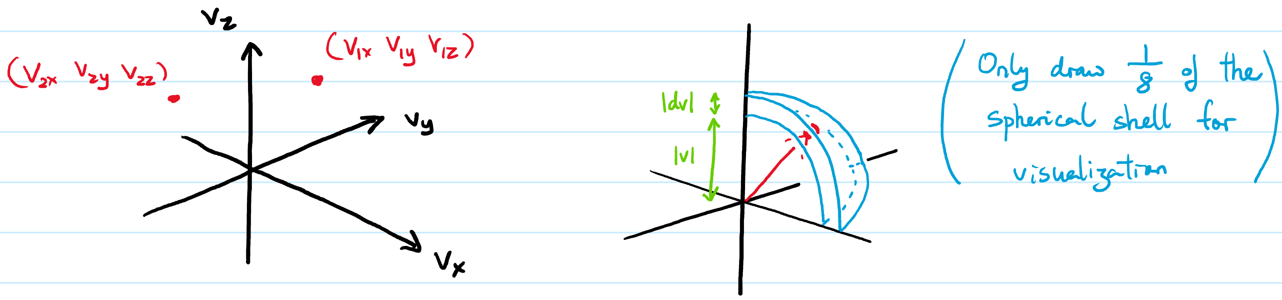
$\Rightarrow$ Different travelling direction

= Different states under the same energy U

= Count as multiplicity of the state with energy U

② This kind of multiplicity is higher for states with larger $|\vec{v}|$

We can visualize this through the space of $\{v_x, v_y, v_z\}$



Every point represents a possible state

Any point (v_x, v_y, v_z) satisfying

$$|v| \leq \sqrt{v_x^2 + v_y^2 + v_z^2} \leq |v + dv|$$

can be found in the spherical shell of radius between $|v|$ & $|v + dv|$

$$\Rightarrow \text{No. of points (states) in the shell} \propto \text{volume of the shell} \ (4\pi r^2 dr)$$

$$\Rightarrow \boxed{\begin{matrix}\text{Multiplicity of states with} \\ |v| \leq \sqrt{v_x^2+v_y^2+v_z^2} \leq |v+dv|\end{matrix} \quad \propto \quad 4\pi |v|^2 d|v|}$$

Change of variable back to U by

$$U = \frac{1}{2} m |v|^2 \quad \Rightarrow \quad |v|^2 = \frac{2U}{m}, \quad d|v| = \sqrt{\frac{1}{2mU}}\, dU$$

$$\boxed{W(U)\,dU = \begin{matrix}\text{Multiplicity of states with} \\ U \leq \text{energy} \leq U + dU\end{matrix} \propto 4\pi \left(\frac{2U}{m}\right) \sqrt{\frac{1}{2mU}}\, dU}$$

③ Hence the probability of states related to energy by

$$P\begin{pmatrix}\text{Ideal gas system} \\ \text{having energy} \\ \text{between } [U, U+dU]\end{pmatrix} dU = \frac{e^{-\frac{U}{kT}}\, W(U)\,dU}{\int_0^\infty e^{-\frac{U}{kT}}\, W(U)\,dU}$$

Interestingly, the denominator can be calculated analytically

$$\int_0^\infty e^{-\frac{U}{kT}} W(U)\,dU = \int_0^\infty e^{-\frac{U}{kT}} \cdot 4\pi\sqrt{\frac{2U}{m^3}}\,dU$$

$$= 4\pi\sqrt{\frac{2}{m^3}} \int_0^\infty e^{-\frac{U}{kT}} \sqrt{\frac{U}{kT}}\,(kT)^{\frac{3}{2}}\, d\left(\frac{U}{kT}\right)$$

Let $x = \frac{U}{kT}$

$$= \frac{8\pi}{\sqrt{2}}\left(\frac{kT}{m}\right)^{\frac{3}{2}} \int_0^\infty e^{-x}\sqrt{x}\,dx$$

$$= \frac{8\pi}{\sqrt{2}}\left(\frac{kT}{m}\right)^{\frac{3}{2}} \cdot \boxed{\frac{\sqrt{\pi}}{2}}$$

This particular kind of integral has analytical soln.

Search for "Gaussian Integral"

$$= 8\left(\frac{\pi kT}{2m}\right)^{\frac{3}{2}}$$

So finally the probability is

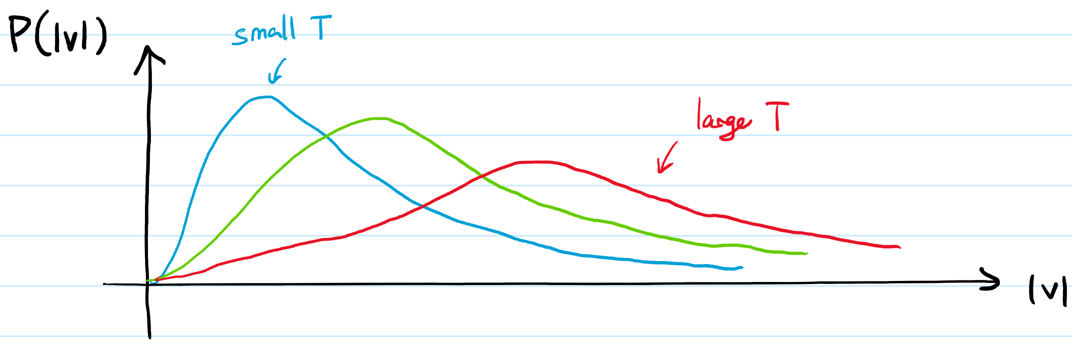
$$P\begin{pmatrix}\text{Ideal gas system} \\ \text{having energy} \\ \text{between } [U, U+dU]\end{pmatrix} dU = \frac{1}{8}\left(\frac{2m}{\pi kT}\right)^{\frac{3}{2}} e^{-\frac{U}{kT}} \cdot 4\pi\sqrt{\frac{2U}{m^3}}\,dU$$

$$= \frac{2}{\sqrt{\pi k^3 T^3}} \sqrt{U}\, e^{-\frac{U}{kT}}\,dU$$

But this is more common to be found expressed in terms of $|v| = \sqrt{\frac{2U}{m}}$

$$P\begin{pmatrix}\text{Ideal gas system} \\ \text{having velocity} \\ \text{between } [|v|, |v+dv|]\end{pmatrix} d|v| = \sqrt{\frac{2m^3}{\pi k^3 T^3}}\, |v|^2 e^{-\frac{m|v|^2}{2kT}}\, d|v|$$

This is the Maxwell-Boltzmann distribution



Average Speed of Ideal gas

In textbook you can usually find 2 kinds of average speed about ideal gas. How are they derived?

① **Average Speed** = Expected value to $|v|$ $E(|v|)$

$$E(|v|) = \int_0^\infty |v| \cdot P(|v|)\, d|v|$$

$$= \int_0^\infty |v| \cdot \sqrt{\frac{2m^3}{\pi k^3 T^3}}\, |v|^2 e^{-\frac{m|v|^2}{2kT}}\, d|v|$$

$$= \sqrt{\frac{2m^3}{\pi k^3 T^3}} \left(\frac{2kT}{m}\right)^2 \cdot \int_0^\infty \left(\sqrt{\frac{m}{2kT}}\, v\right)^3 e^{-\left(\sqrt{\frac{m}{2kT}}\, v\right)^2} d\left(\sqrt{\frac{m}{2kT}}\, v\right)$$

Let $x = \sqrt{\frac{m}{2kT}}\, v$

$$= \sqrt{\frac{32kT}{\pi m}} \int_0^\infty x^3 e^{-x^2}\, dx$$

$$= \sqrt{\frac{32kT}{\pi m}} \cdot \frac{1}{2}$$

Just integration by part

$$= \sqrt{\frac{8kT}{\pi m}}$$

② **Root Mean Square Speed** = $\sqrt{\text{Expected value to } |v|^2}$ $\sqrt{E(|v|^2)}$

$$E(|v|^2) = \int_0^\infty |v|^2 \cdot P(|v|)\, d|v|$$

$$= \int_0^\infty |v|^2 \cdot \sqrt{\frac{2m^3}{\pi k^3 T^3}}\, |v|^2 e^{-\frac{m|v|^2}{2kT}}\, d|v|$$

$$= \sqrt{\frac{2m^3}{\pi k^3 T^3}} \left(\frac{2kT}{m}\right)^3 \cdot \int_0^\infty \left(\sqrt{\frac{m}{2kT}}\,v\right)^4 e^{-\left(\sqrt{\frac{m}{2kT}}v\right)^2} d\left(\sqrt{\frac{m}{2kT}}\,v\right)$$

$$= \sqrt{\frac{64k^2T^2}{\pi m^2}} \int_0^\infty x^4 e^{-x^2} dx$$

Let $x = \sqrt{\frac{m}{2kT}}\,v$

$$= \sqrt{\frac{64k^2T^2}{\pi m^2}} \cdot \frac{3\sqrt{\pi}}{8}$$

This requires Gaussian Integral

$$= \frac{3kT}{m}$$

$\therefore$ Root mean square speed $= \sqrt{E(|v|^2)} = \sqrt{\frac{3kT}{m}}$

☆☆ Because Average KE $= E\left(\frac{1}{2}m|v|^2\right)$

$$= \frac{1}{2}m\,E(|v|^2)$$

$$= \frac{1}{2}m\,v_{rms}^2$$

So the root mean square speed is used far more commonly