CHM 421/621 Statistical Mechanics

Lecture 16 Review of Probability Theory - I

Introduction and Review

Lecture Plan

Review of probability theory

- Definitions of simple and compound events
- Frequency and probability
- *A priori* and *a posteriori* probabilities
- Disjoint and non-disjoint distributions
- Conditional Probabilities and Independent events

Definitions: Simple Event

Simple Event: Distinct or mutually exclusive results of an experiment.

E.g. Tossing a coin: 2 simple events possible (H/T)
A single die is rolled: 6 simple events possible

Frequency: The ratio of the number of times a simple event occurs to the total number of times the experiment is performed.

E.g. A coin is tossed 10 times and the result H occurs 4 times. Then the frequency of occurrence of H in the experiment is $f_H = 2/5$

The frequency of a particular event might depend on the number of times the experiment is conducted.

It is, however, desirable to associate a characteristic number with the event that does not depend on the number of trials.

Definitions: Probability

Probability of a simple event:

$$P_i = \lim_{N \to \infty} f_i(N) = \lim_{N \to \infty} \frac{n_i(N)}{N}$$

Two possible interpretations:

(1) Carrying out *N* successive expts. on the same system. (e.g. *via* time evolution of system)

(2) Carrying out 1 expt. each on *N* identically prepared (macroscopically indistinguishable) systems. => **Ensemble**

Ergodic Hyopthesis: Either approach would yield the same probability of the event.

Inherent properties of probability:

(1) For any event *i*: $P_i \geq 0$

(2) Normalisation: $\sum_{i \in \mathrm{all}} P_i = 1$

A priori probabilities

If there is no apparent reason for one simple event to occur more frequently than any other then we can assume that their probabilities are all equal.

In such a case, if there are totally *M* events possible, then the above properties imply that

$$P_i = \frac{1}{M} \;\; \forall \; i \in \{1, M\}$$

e.g. Throwing a single die: numbers occur with probability 1/6
Tossing an unbiased coin: H/T occur with probability 1/2
Picking any particular card from a deck of 52 cards: ?

If we have no information about the system then it is only fair to assume that all simple events are equally likely.

Probabilities calculated from such assumptions (without measurements) are termed as ***a priori*** probabilities.

A posteriori probabilities

Probabilities obtained from actual measurements are termed as ***a posteriori*** probabilities

When we set about calculating properties of macroscopic systems we will only know for certain the values of the macroscopic constraints (e.g. p,V,T,N) we impose on them. We would have no reason to favour less any microstate over others as long as they all conform to the constraints imposed.

Thus, **in statistical mechanics** we shall make the **assumption of equal *a priori* probabilities for micro states consistent with the macroscopic constraints**.

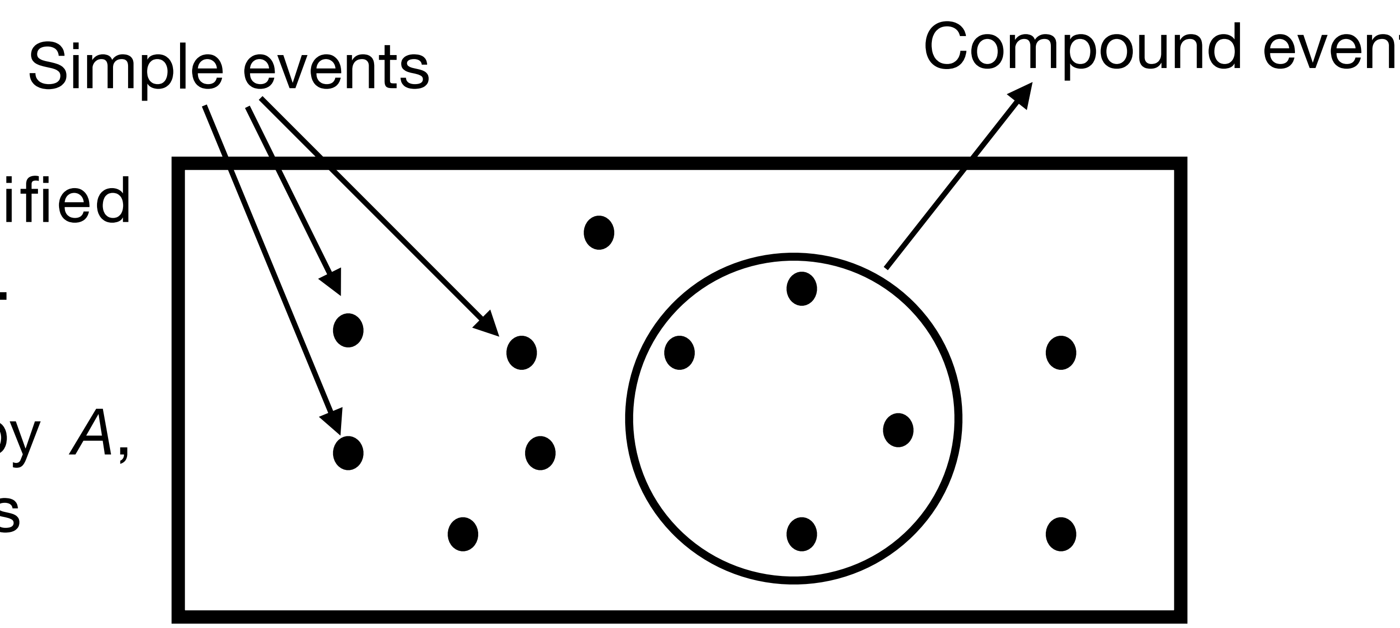
Definitions: Compound Events

Simple events can be thought of as points in a "sample space".

Compound Events: Any specified collection of points in sample space.

If we denote a compound event by *A*, then probability of occurrence of *A* is

$$P(A) := \sum_{i \in A} P_i$$



Compound Events: Example

What is the probability that a card drawn from a deck of 52 cards will have a ♥ on it?

Solution:

Each card in the deck has the same *a priori* probability 1/52

There are 13 cards with ♥ on them.

Therefore,

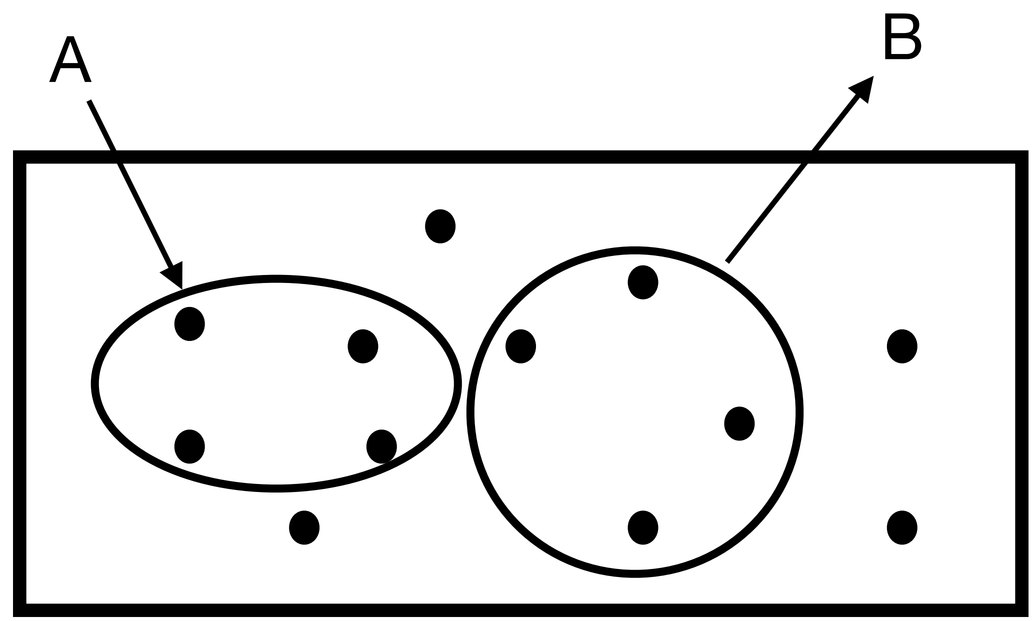
$$P(\heartsuit) = \sum_{i \in \heartsuit} P_i$$

$$= 13 \times \frac{1}{52} = \frac{1}{4}$$

Definitions: Disjoint Events

Two compound events without a point in common are termed **disjoint**.

$$P(A \ \cup \ B) = P(A) + P(B)$$

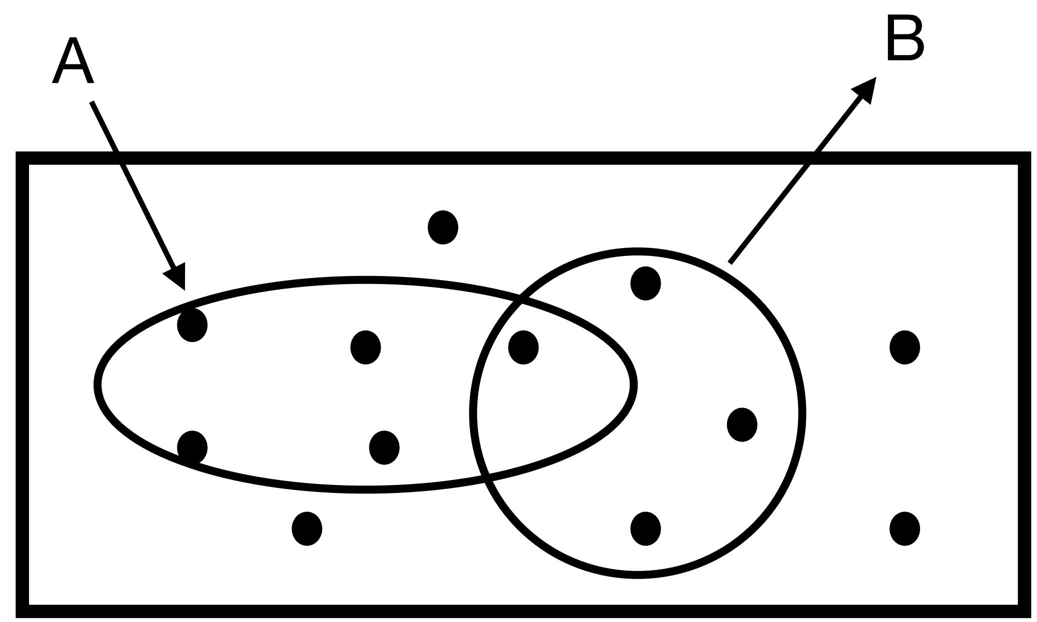


Probability of a picked card being ♥ or ♠

Definitions: Non-disjoint Events

Two compound events with points in common are termed **non-disjoint.**

$$P(A \ \cup \ B) = P(A) + P(B) - P(A \ \cap \ B)$$



Probability of a picked card having the number 3 or ♥

Definitions: Conditional Probability

We will often be interested in events which occur under certain conditions.

Conditional probability measures the effect (if any) of the occurrence of an event *A* when it is known that event *B* has occurred in the expt.

E.g. What's the probability of a card drawn having ❤️ given that it is a one-eyed jack?

$$P(X|Y) := \frac{P(XY)}{P(Y)}$$

When the two events are **independent** we have $P(X|Y)P(Y) = P(Y|X)P(X)$

Or

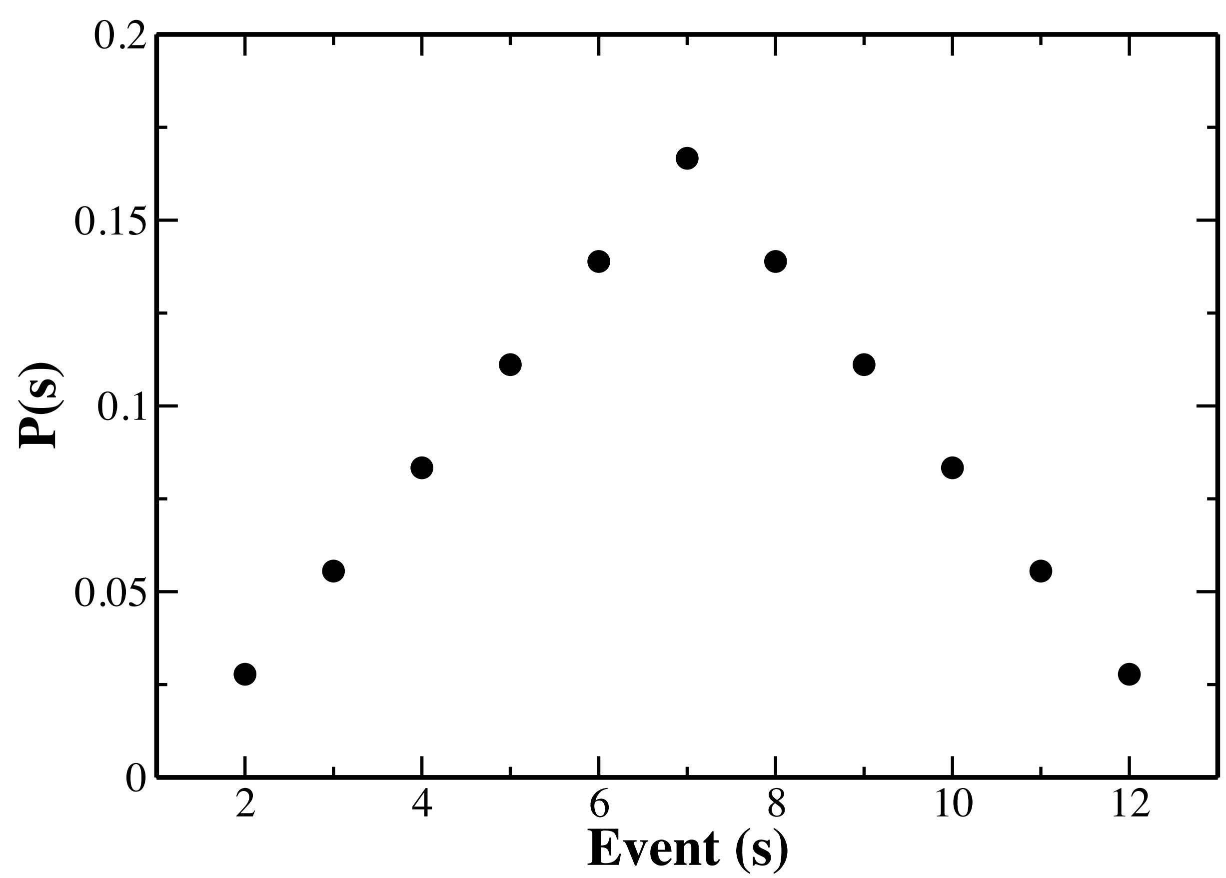
$$\boxed{P(XY) = P(X)P(Y)}$$

Probability Distributions

Discrete events

When 2 dice are rolled together, what is the probability that the sum of the resulting numbers is *s* ?

s	2	3	4	5	6	7	8	9	10	11	12
P(s)	1/36	1/18	1/12	1/9	5/36	1/6	5/36	1/9	1/12	1/18	1/36



Probability is a function of *s*

P(*s*) is called a **probability distribution function**

Note that,

$$P(s) \geq 0$$

$$\sum_s P(s) = 1$$

Probability Distributions

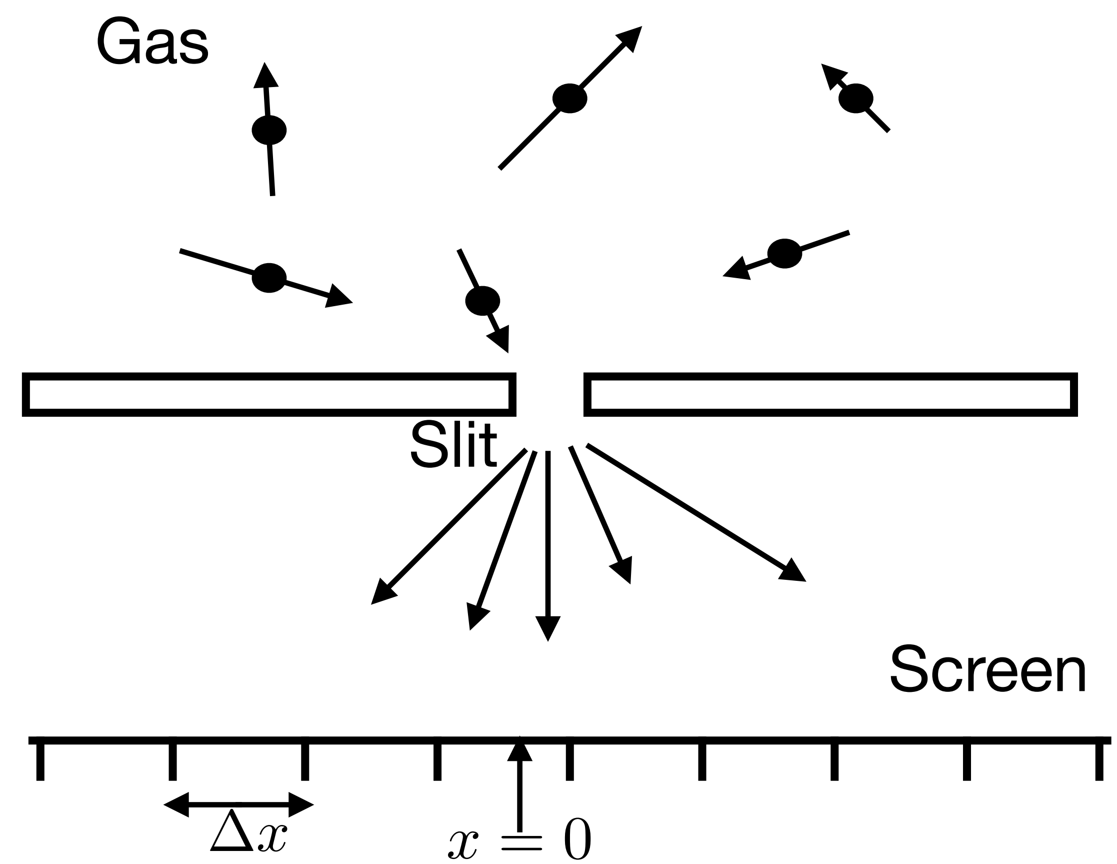
Continuous events

A gas in a contained at temperature *T* and pressure *P* is allowed to escape, via a small slit made on one of the walls, in to vaccuum.

The escaping molecule is allowed to encounter a screen with a detector.

The direction of motion of the molecule can be determined by the position of detection on the screen and the location of the slit.

What is the probability that an escaping molecule was traveling in a certain direction?



The event here is *x* and is continuously distributed on the screen.

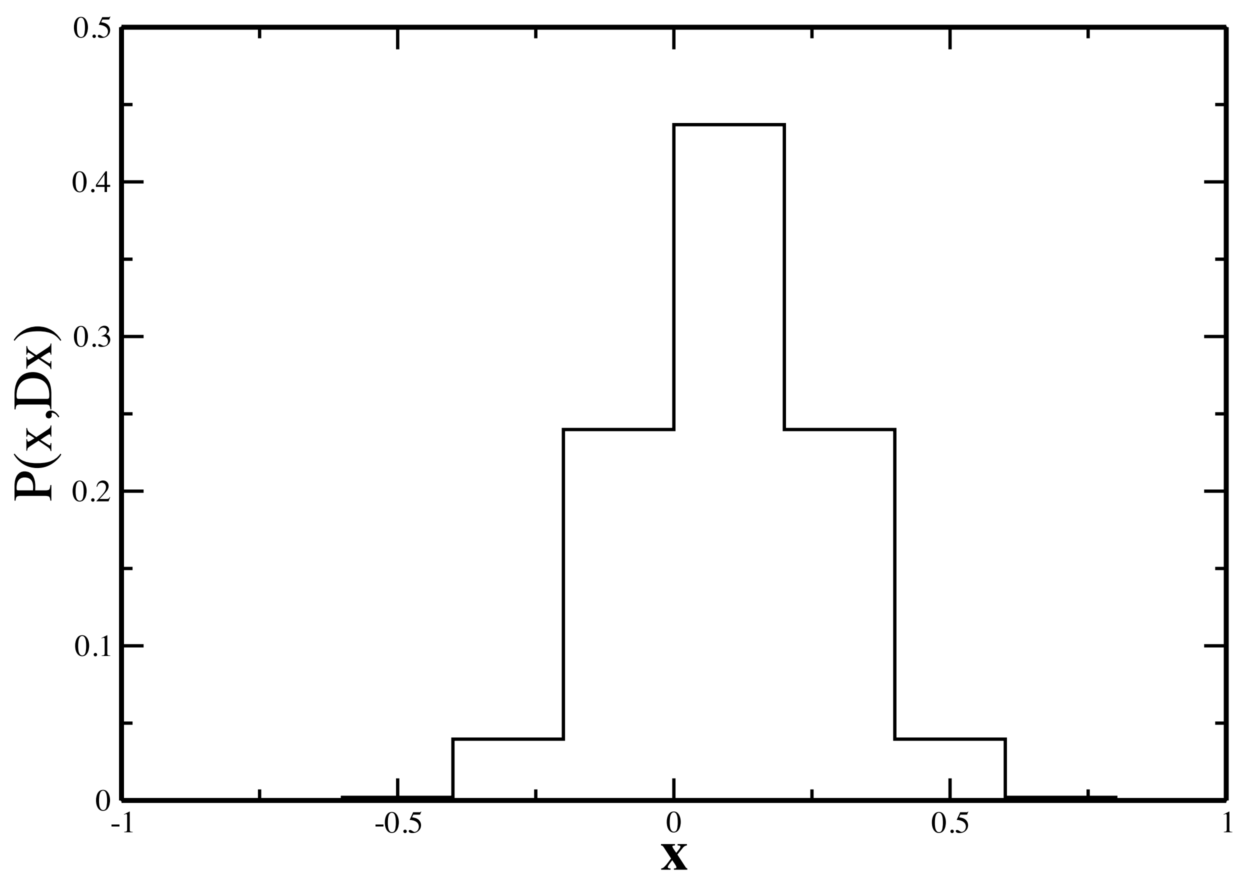
Note that, the probability of a molecule landing at a particular point on the screen is zero!

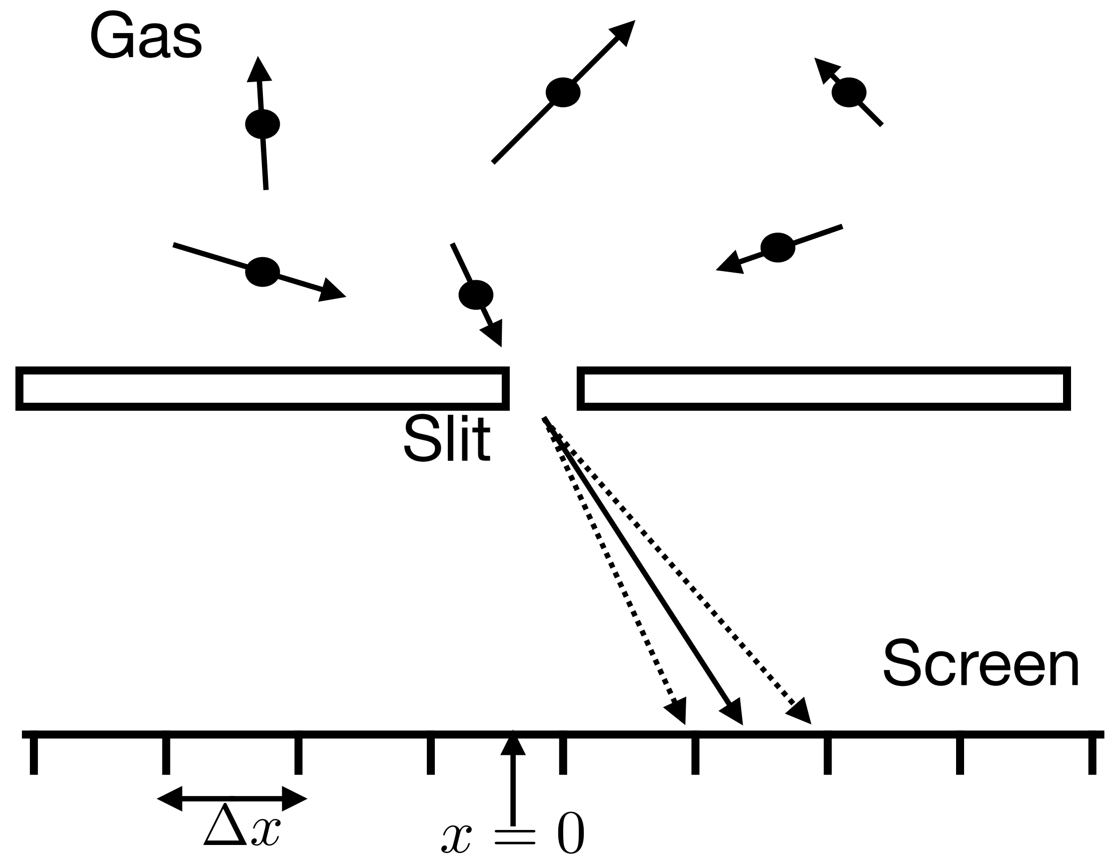
Probability Distributions

Continuous events

We can only measure the likelihood of a molecule landing in a particular "detector bin".

This will result in a histogram.





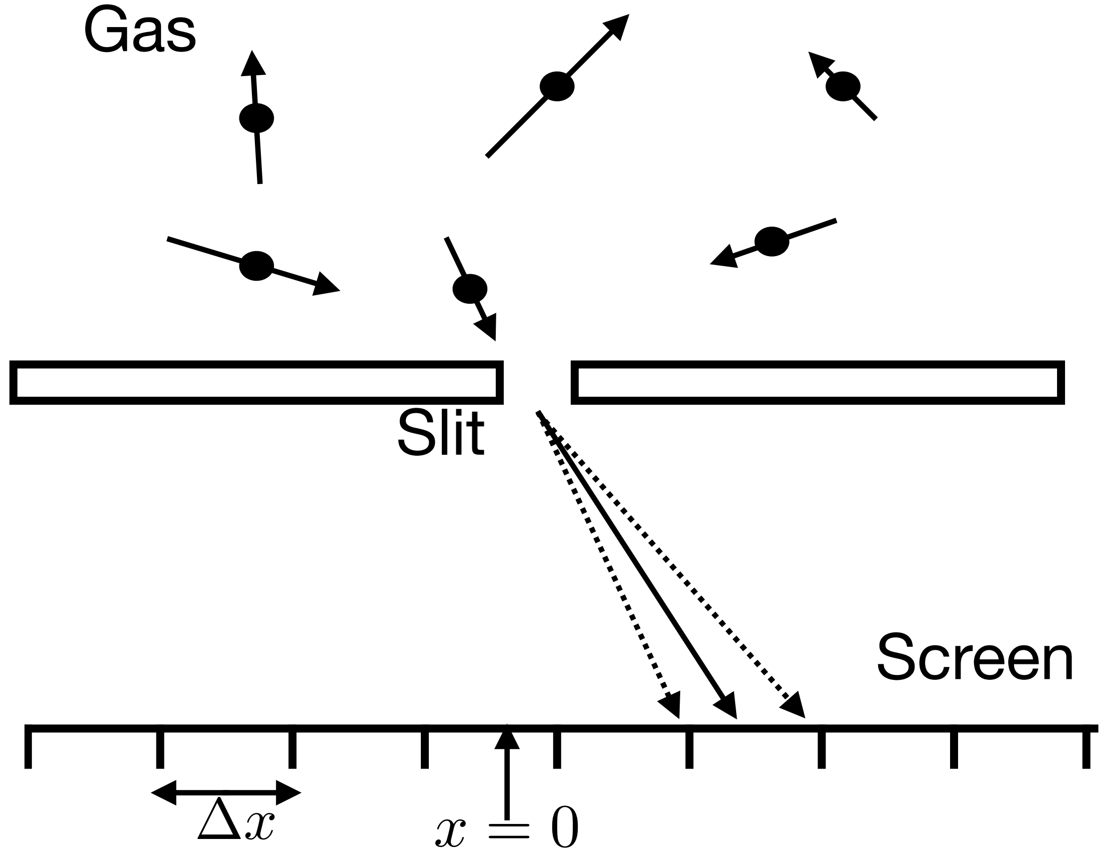
$P(x, \Delta x)$

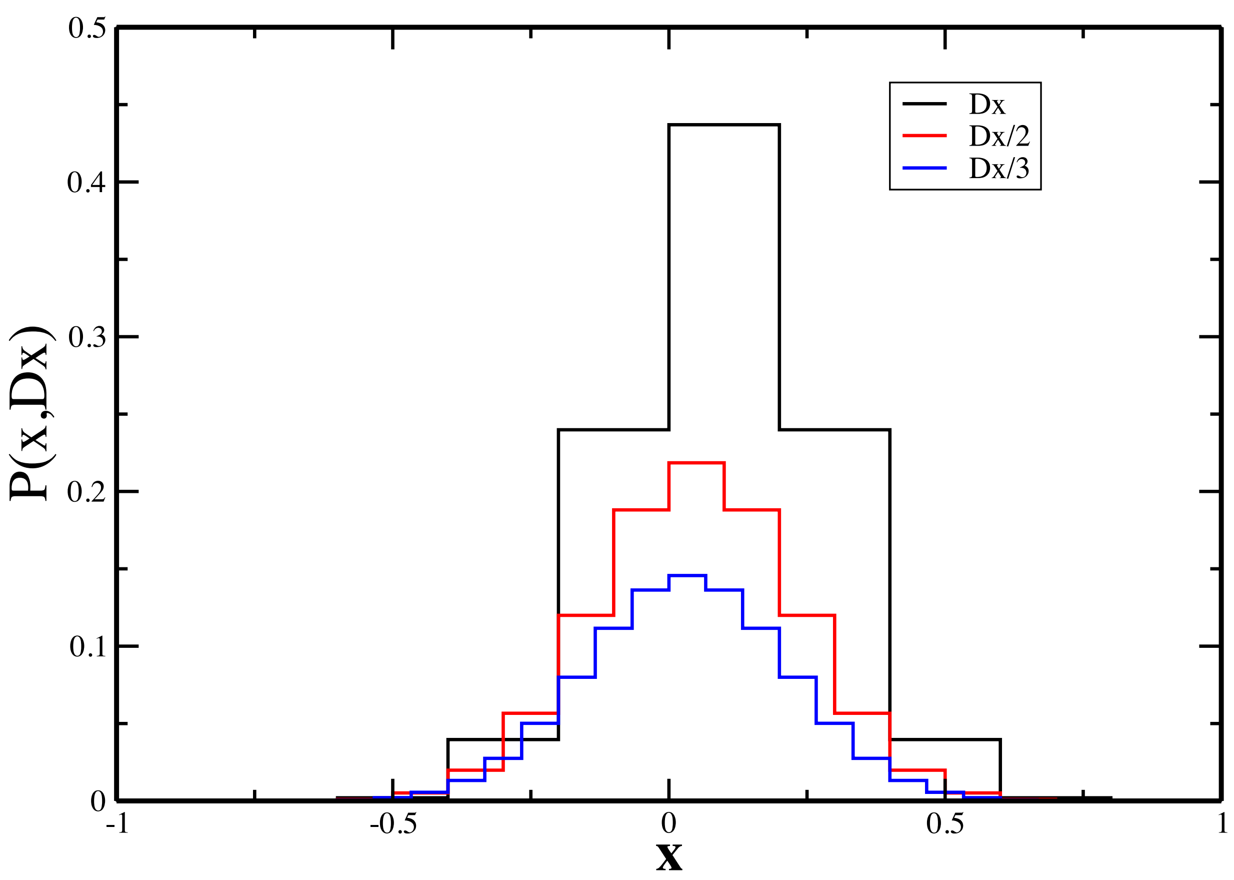
= probability that a molecule will strike the strip of width Dx whose centre is *x*

Probability Distributions

Continuous events

The histogram gets sharper if we increase the resolution of the detector.





$P(x, \Delta x)$

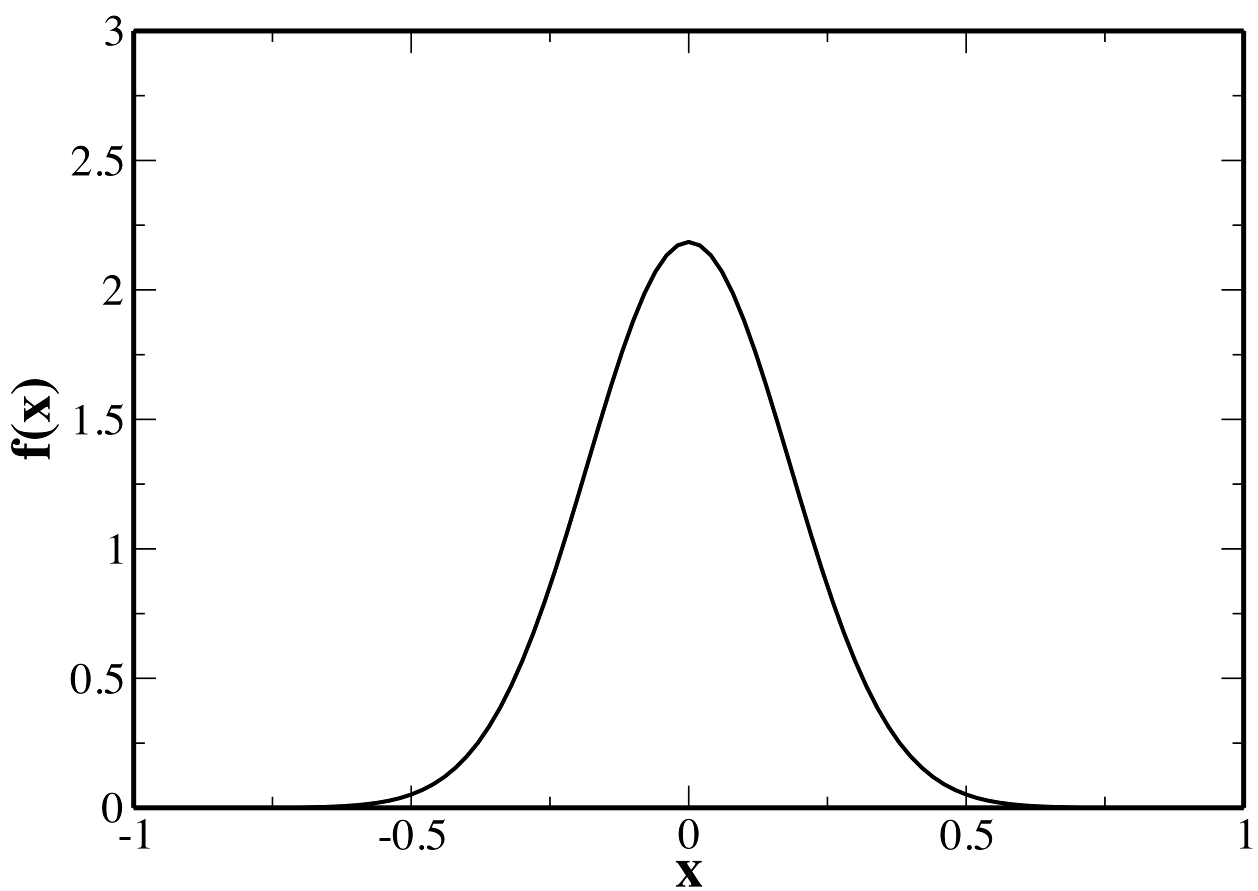
= probability that a molecule will strike the strip of width Dx whose centre is *x*

Probability Distributions

Continuous events

In the limit of fine resolution we can define the distribution function:

$$f(x) = \lim_{\Delta x \to 0} \frac{P(x, \Delta x)}{\Delta x}$$



$$f(x)\ dx$$

= probability that a molecule will strike the detector between *x* and *x+dx*

Properties:

$$f(x) \geq 0$$

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

Probability Distributions

Continuous events

Probable number of molecules that will strike the screen between *x* and *x+dx*

$$F(x)\ dx = N\ f(x)\ dx$$

$$\int_{-\infty}^{\infty} F(x)\ dx = N$$

Where *N* is the total number of molecules in the gas. Here, we have assumed that the arrival events of each molecule at the screen are independent.