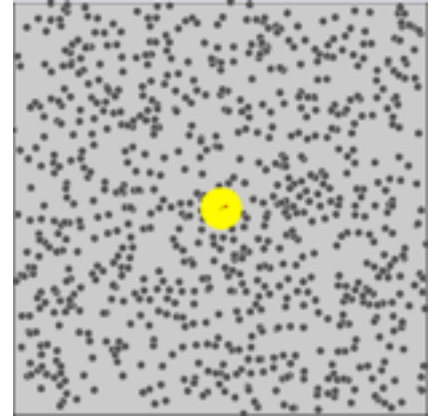


Lecture 4: Diffusion: The Macroscopic and Microscopic Theories

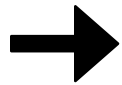
R. Ranganathan

Green Center for Systems Biology, ND11.120E

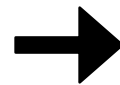
Spontaneous movement of particles due to thermal agitation



Robert Brown
1827



Adolf Fick
1855



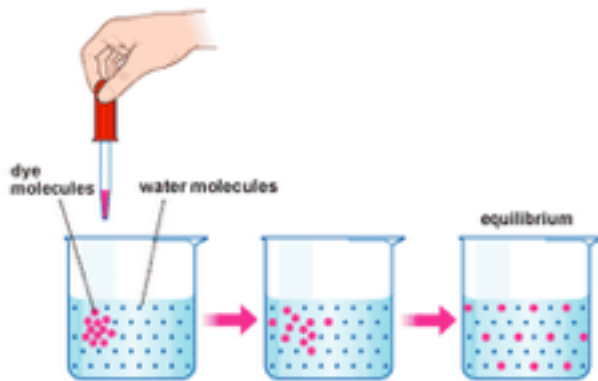
Albert Einstein
1905

Linear systems at the thermodynamic limit....

	$n = 1$	$n = 2$ or 3	$n \gg 1$	continuum
Linear	exponential growth and decay	second order reaction kinetics	electrical circuits	Diffusion Wave propagation quantum mechanics viscoelastic systems
	single step conformational change	linear harmonic oscillators	molecular dynamics	
	fluorescence emission	simple feedback control	systems of coupled harmonic oscillators	
	pseudo first order kinetics	sequences of conformational change	equilibrium thermodynamics	
Nonlinear	fixed points	anharmonic oscillators	systems of non-linear oscillators	Nonlinear wave propagation Reaction-diffusion in dissipative systems Turbulent/chaotic flows
	bifurcations, multi stability	relaxation oscillations	non-equilibrium thermodynamics	
	irreversible hysteresis	predator-prey models	protein structure/function	
	overdamped oscillators	van der Pol systems	neural networks	
		Chaotic systems	the cell	
			ecosystems	

First, the macroscopic view...

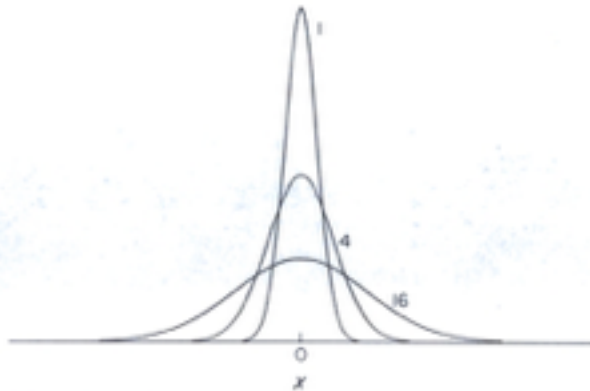
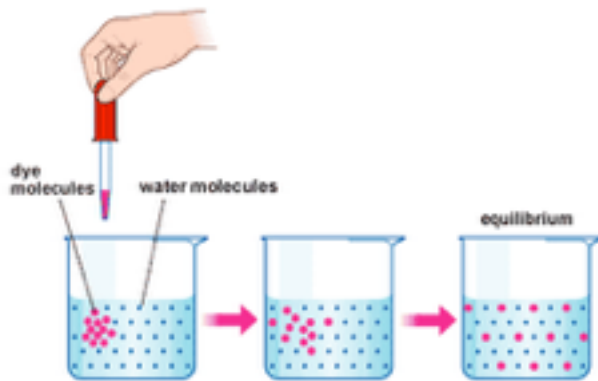
The observations:



i) Particles confined at one place initially
tend to spread out spontaneously

First, the macroscopic view...

The observations:



- i) Particles confined at one place initially tend to spread out spontaneously
- ii) The spatial distribution looks like a bell curve for all times.
- iii) The mean displacement of particles shows that they go nowhere!
- iv) How far the particles spread out (the RMS displacement) goes as the square root of time.

First, the macroscopic view...

The physical model:

~1880's: There is a "force" that makes like particles repel or that makes un-like particles attract.

So, like electrostatics, gravitation, or thermal conductivity [Fourier's heat equations] it was proposed that the flux of molecules is proportional to the "force".

$$J = D \frac{dc}{dx}$$

, in 1-D.

Fick's 1st Law

First, the macroscopic view...

The physical model:

“The first task would now be to deduce the basic law for this process of diffusion from the general laws of motion.... Indeed, one will admit that from start to finish nothing may be more likely than this: that the spread of a dissolved body in a solvent...proceeds according to the same law which Fourier has established for the spread of heat in a conductor; and which Ohm has transferred with such splendid success to the spread of electricity. One need only substitute in Fourier’s law the words quantity of heat with the words quantity of dissolved body, and the word temperature with density of solution”. (A. Fick, 1855; adapted from Agutter et al. (2001), J. Hist. Biol. 33: 71-111)

$$J = -D \frac{dc}{dx} \quad , \quad \text{in } 1-D \quad \text{Fick's 1st Law}$$

But then, along came Einstein in 1905....

The physical model:

He showed that all particles at temperature T have an average kinetic energy in every dimension of $kT/2$

Thus...

$$\left\langle \frac{mv_x^2}{2} \right\rangle = \frac{kT}{2}$$

in 1D.

From this ...

$$\sqrt{\langle v_x^2 \rangle} = \sqrt{kT/m}$$

\Rightarrow rms velocity of a particle with mass m .

For a lysozyme molecule \rightarrow

$$1.3 \times 10^3 \text{ cm/s} \quad !!$$

But then, along came Einstein in 1905....

The physical model:

But, in aqueous solution, it keeps bumping into H_2O molecules, and always (and randomly) changes direction.

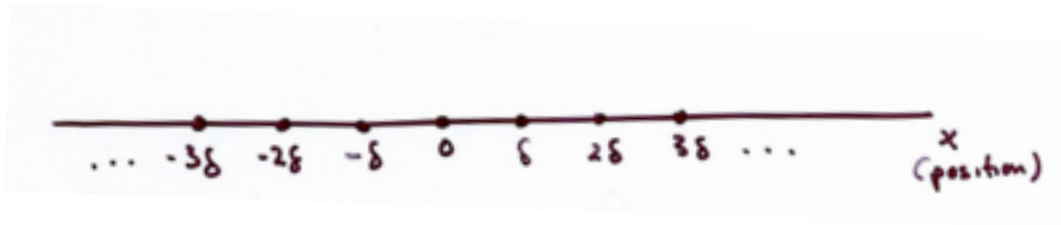
It wanders around with the following properties:

- ① The probability of going a new direction is independent of the ~~per~~ current direction. It forgets one direction right away.
- ② Directions are chosen randomly with no bias.

⇒ An unbiased random walk

How does this explain the phenomenological properties of diffusion?

Does the (unbiased) random walk account for all these properties? Let's look in 1-D....



The rules of the random walk:

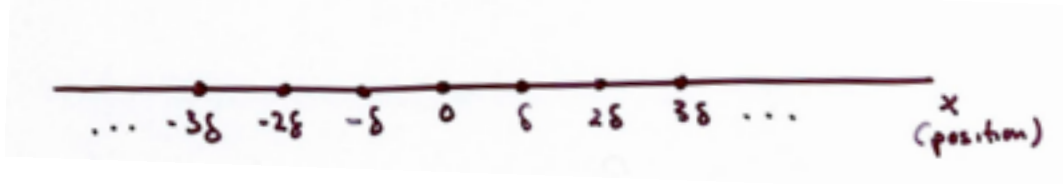
- ① Each particle steps to the right or left once every τ seconds, at a velocity ($\pm v_x$). The distance moved is

$$\delta = \pm v_x \tau$$

- ② The probability of going either way is equal ($\frac{1}{2}$), and each step is statistically independent.
- ③ Each particle is independent of others.

What are the consequences?

1. The average displacement of particles....



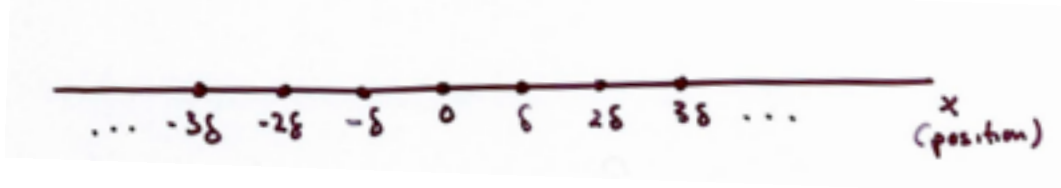
Each step takes τ seconds, distance moved is δ

First what is the position of each particle i after n steps of the walk? Well....

$$x_i(n) = x_i(n-1) \pm \delta$$

A “stochastic iterative map”....we will come back to this.

1. The average displacement of particles....



Each step takes τ seconds, distance moved is δ

First what is the position of each particle i after n steps of the walk? Well....

$$x_i(n) = x_i(n-1) \pm \delta$$

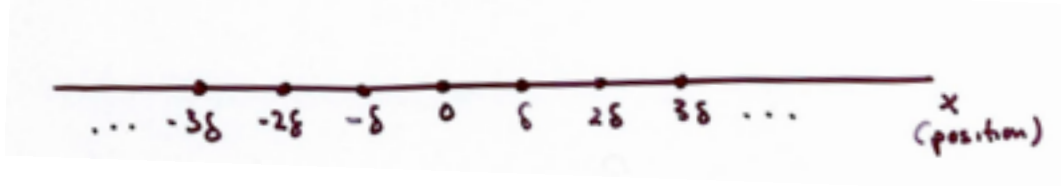
The average position of all N particles:

$$\begin{aligned} \langle x(n) \rangle &= \frac{1}{N} \sum_{i=1}^N x_i(n) \\ &= \frac{1}{N} \sum_{i=1}^N [x_i(n-1) \pm \delta] \\ &= \frac{1}{N} \sum_{i=1}^N x_i(n-1) \\ &= \langle x(n-1) \rangle \end{aligned}$$

Thus, the particles go nowhere on average



2. How much do the particles spread out over time?



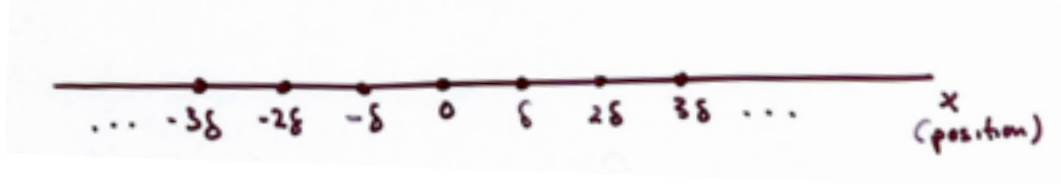
Each step takes τ seconds, distance moved is δ

We want the RMS displacement: $\sqrt{\langle x_i^2(n) \rangle}$

First what is the squared position of each particle i after n steps? Well....

$$\begin{aligned}x_i^2(n) &= [x_i(n-1) \pm \delta]^2 \\ &= x_i^2(n-1) \pm 2\delta x_i(n-1) + \delta^2\end{aligned}$$

2. How much do the particles spread out over time?



Each step takes τ seconds, distance moved is δ

We want the RMS displacement: $\sqrt{\langle x_i^2(n) \rangle}$

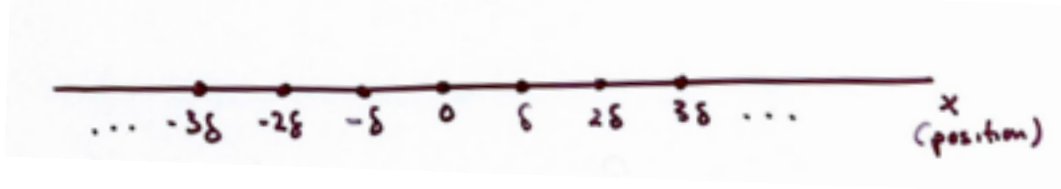
First what is the squared position of each particle i after n steps? Well...

$$\begin{aligned}x_i^2(n) &= [x_i(n-1) \pm \delta]^2 \\ &= x_i^2(n-1) \pm 2\delta x_i(n-1) + \delta^2\end{aligned}$$

Now, let's take the average...

$$\langle x_i^2(n) \rangle = \frac{1}{N} \sum_{i=1}^N [x_i^2(n-1) \pm 2\delta x_i(n-1) + \delta^2]$$

How much do particles spread out over time?



Each step takes τ seconds, distance moved is δ

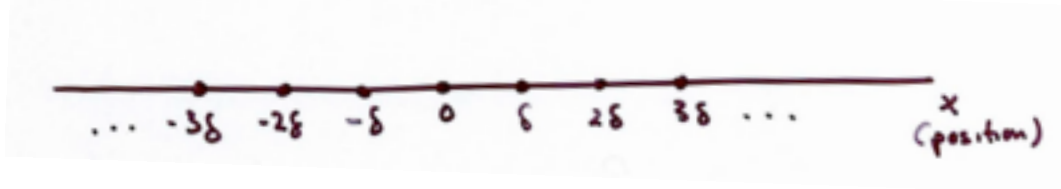
We want the RMS displacement: $\sqrt{\langle x_i^2(n) \rangle}$

$$\langle x_i^2(n) \rangle = \frac{1}{N} \sum_{i=1}^N [x_i^2(n-1) + 2\delta x_i(n-1) + \delta^2]$$

$$= \frac{1}{N} \sum_{i=1}^N x_i^2(n-1) + \delta^2$$

$$= \langle x_i^2(n-1) \rangle + \delta^2$$

How much do particles spread out over time?



Each step takes τ seconds, distance moved is δ

We want the RMS displacement: $\sqrt{\langle x_i^2(n) \rangle}$

We can simplify....

$$\langle x_i^2(n) \rangle = \langle x_i^2(n-1) \rangle + \delta^2$$

we defined $x_i(0) = 0$, so ...

$$\langle x_i^2(0) \rangle = 0$$

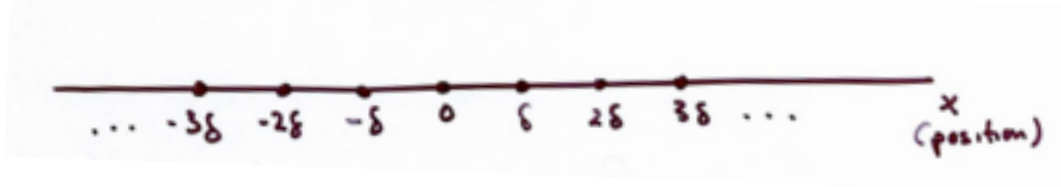
$$\langle x_i^2(1) \rangle = \delta^2$$

$$\langle x_i^2(2) \rangle = 2\delta^2$$

\vdots

$$\langle x_i^2(n) \rangle = n\delta^2 \text{ [after } n \text{ steps]}$$

How much do particles spread out over time?



Each step takes τ seconds, distance moved is δ

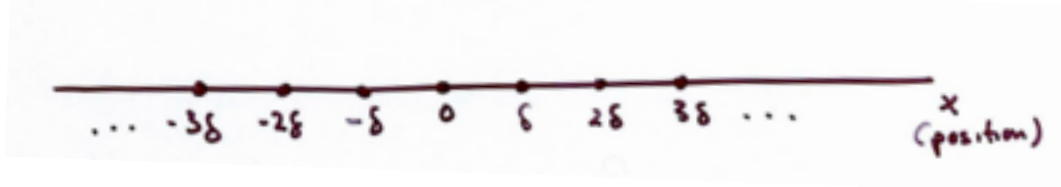
We want the RMS displacement: $\sqrt{\langle x_i^2(n) \rangle}$

We need to change n into time....

$$\begin{aligned} \text{Now } t = n\tau, \text{ so } \dots \\ \langle x^2(t) \rangle &= \left(\frac{t}{\tau}\right) \delta^2 \\ &= \left(\frac{\delta^2}{\tau}\right) t \end{aligned}$$

But...we want the RMS displacement,
so....

How much do particles spread out over time?



Each step takes τ seconds, distance moved is δ

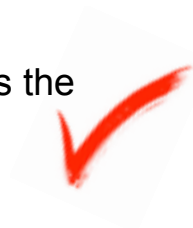
We want the RMS displacement: $\sqrt{\langle x_i^2(n) \rangle}$

We need to change n into time....

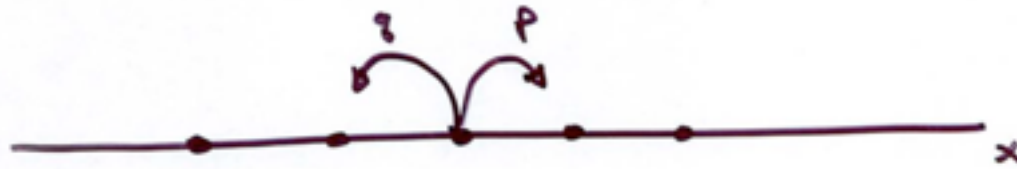
$$\begin{aligned} \text{Now } t = n\tau, \text{ so } \dots \\ \langle x^2(t) \rangle &= \left(\frac{t}{\tau}\right) \delta^2 \\ &= \left(\frac{\delta^2}{\tau}\right) t \end{aligned}$$

$$\sqrt{\langle x^2(t) \rangle} = \sqrt{\left(\frac{\delta^2}{\tau}\right) t}$$

Thus, the particles spread out as the square root of time...



3. What about the shape of the distribution of particles?



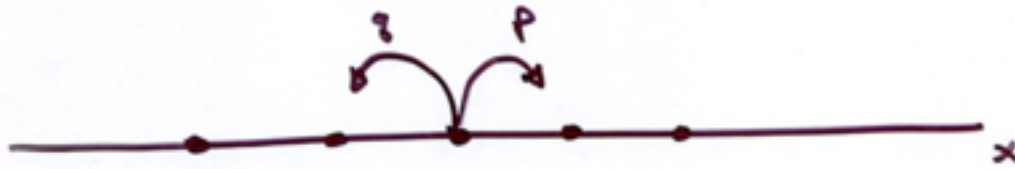
$p =$ probability of going right

$q = 1 - p =$ probability of going left.

What is the probability that a particle steps k times to the right in n trials?

Think about coin tossing....

What about the shape of the distribution of particles?



p = probability of going right

$q = 1 - p$ = probability of going left.

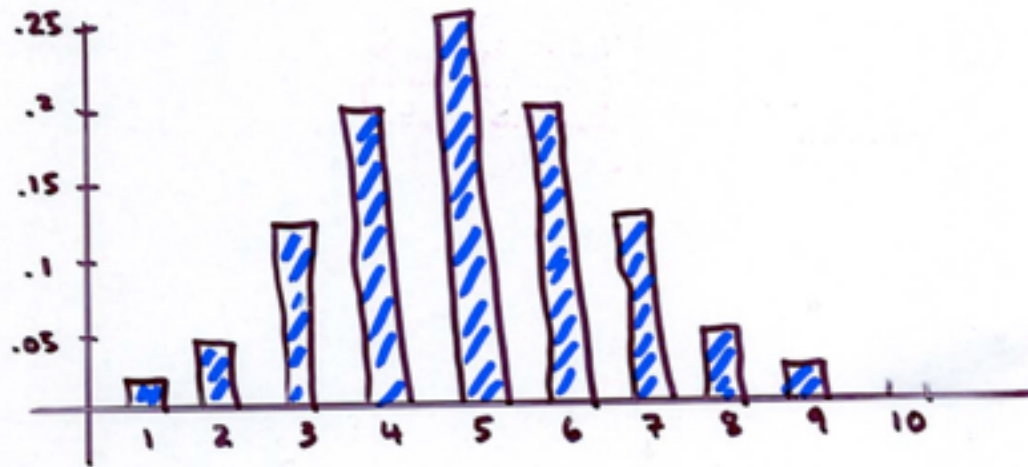
What is the probability that a particle steps k times to the right in n trials?

$$P(k; n, p) = \frac{n!}{k!(n-k)!} p^k q^{n-k}$$

This is the **binomial density function** again,....

What about the shape of the distribution of particles?

This is the binomial density function ... say $p=0.5$. What is the probability of getting 1, 2, 3 ... 10 times to the right out of 10 total trials?



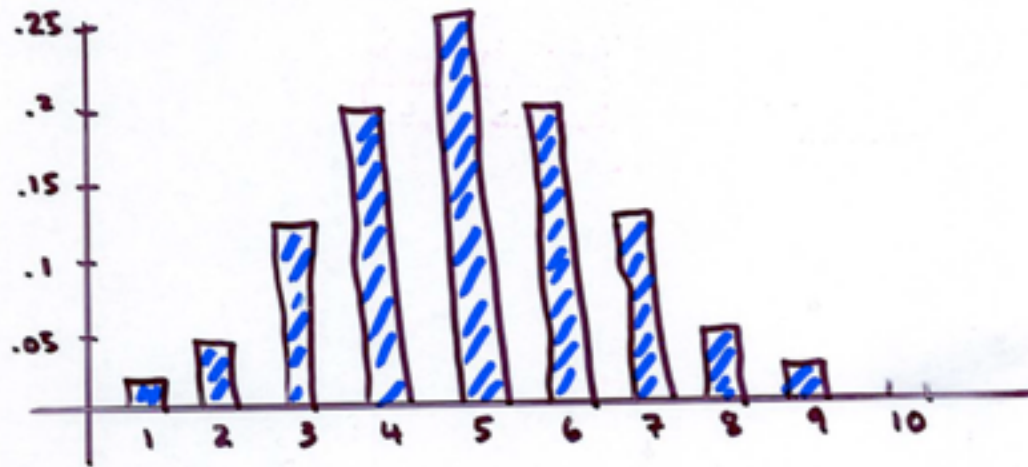
Very reasonably, the most likely outcome is the case of $k=5$.

$$\text{mean} = np$$

$$\text{standard deviation} = np(1-p)$$

What about the shape of the distribution of particles?

This is the binomial density function say $p=0.5$. What is the probability of getting 1, 2, 3 ... 10 times to the right out of 10 total trials?



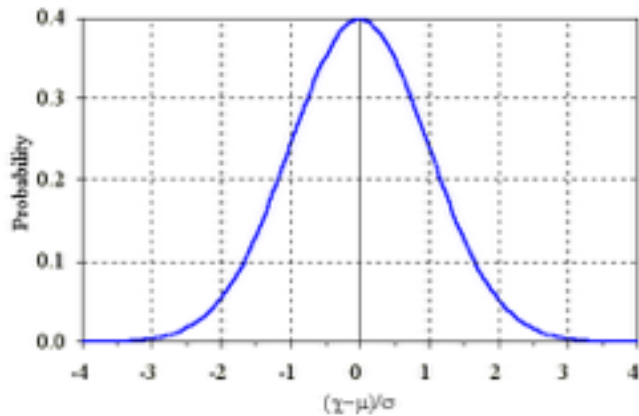
But if the number of trials is very large and p is not too small.....

What about the shape of the distribution of particles?

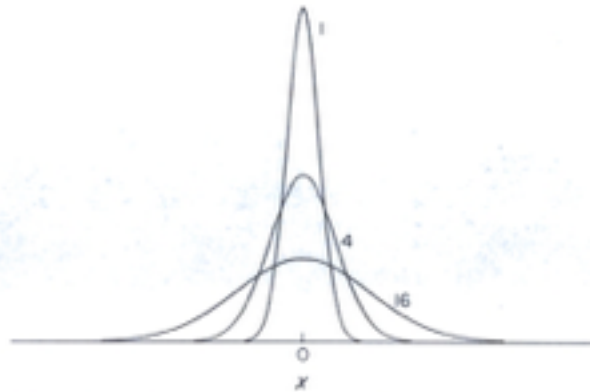
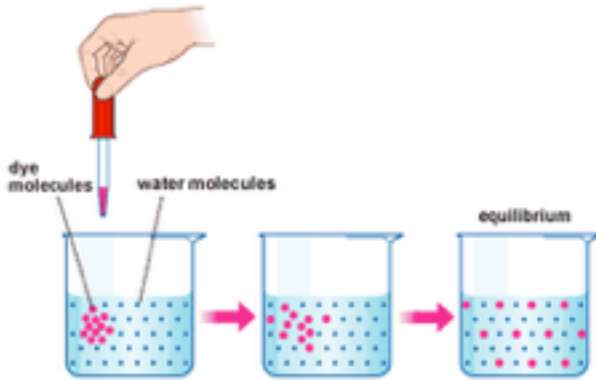
But if the number of trials is very large and p is not too small.....the binomial distribution approaches the Gaussian distribution. The bell shaped curve!



$$P(k) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(k-\mu)^2}{2\sigma^2}}$$



So the random walk does indeed account for the motion of particles...



i) Particles confined at one place initially tend to spread out spontaneously

ii) The spatial distribution looks like a bell curve for all times.

iii) The mean displacement of particles shows that they go nowhere!

iv) How far the particles spread out (the RMS displacement) goes as the square root of time.

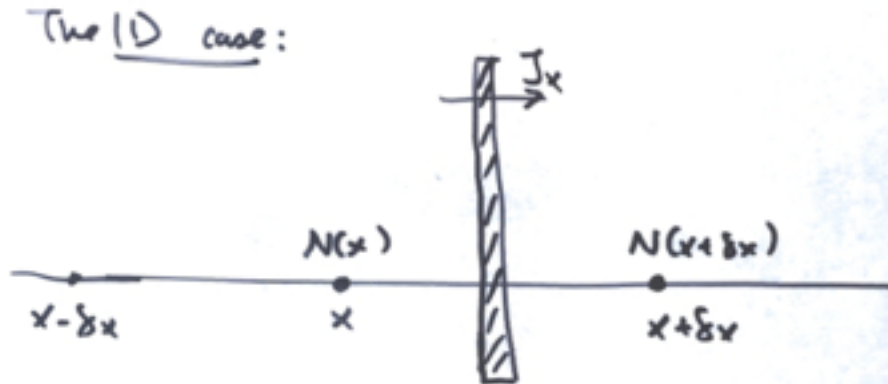
A seminal example of how simple physical theory (the random walk) can explain the rather complex behavior of particles moving under thermal agitation...

So the random walk does indeed account for the motion of particles...

$$J = -D \frac{dc}{dx} \quad , \quad n = 1-D \quad \text{Fick's 1st Law}$$

But, what happened to good old **Fick's Law**, which does indeed also account for the properties of diffusion? Well, it works and it still works with this new understanding....

The relationship of the random walk (the microscopic view) to Fick's first law (the macroscopic view).

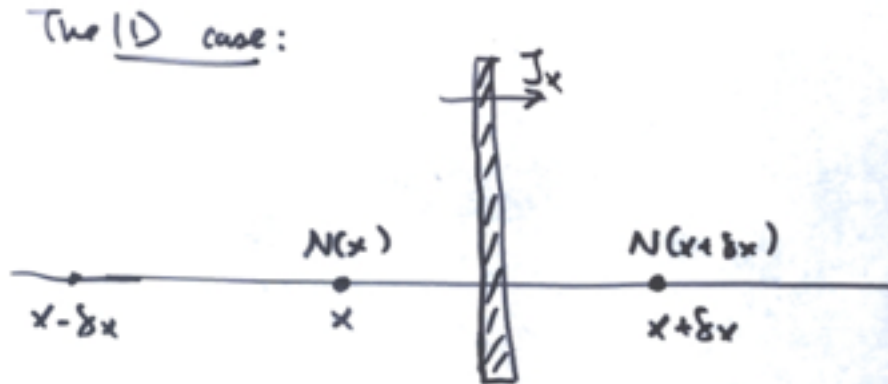


14

$N(x)$ particles at position x ; at each tick of the clock, let's say ~~half~~ the molecules at $N(x)$ jump equally to $x + \delta x$ and $x - \delta x$.
The area of the barrier is A , and the clock ticks every τ sec.

Now, how do we write the flux of particles going from x to $x + \delta x$?

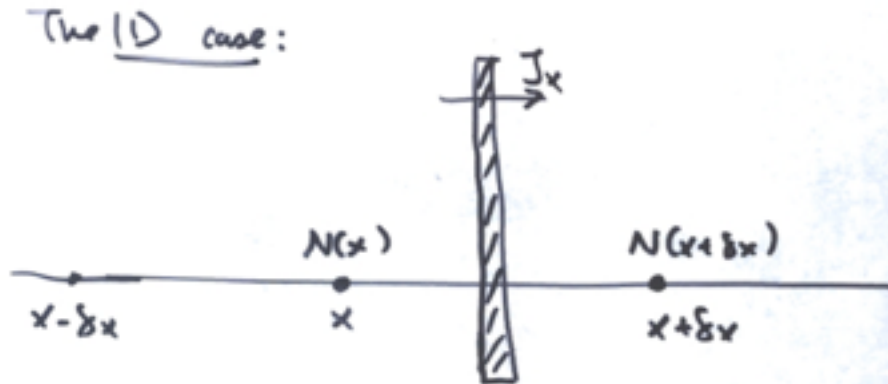
The relationship of the random walk (the microscopic view) to Fick's first law (the macroscopic view).



$$N_{x \rightarrow x + \delta x} = \frac{1}{2} N(x) - \frac{1}{2} N(x + \delta x)$$
$$= -\frac{1}{2} [N(x + \delta x) - N(x)]$$

$$J_x = \frac{\text{No. crossing}}{A \tau} = -\frac{1}{2} \left[\frac{N(x + \delta x) - N(x)}{A \tau} \right]$$

The relationship of the random walk (the microscopic view) to Fick's first law (the macroscopic view).

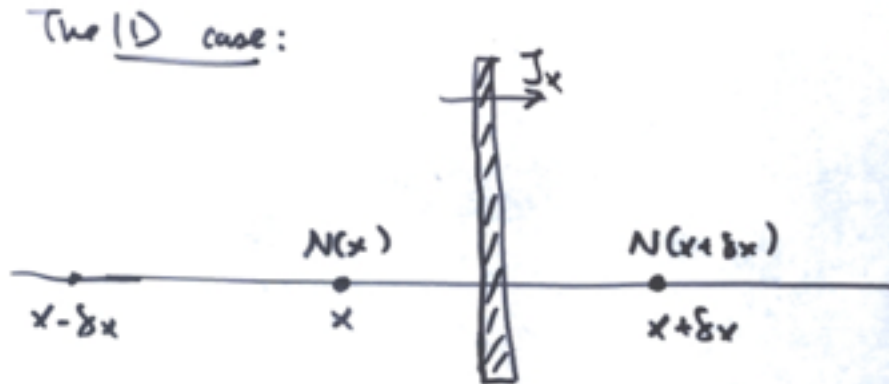


$$N_{x \rightarrow x + \delta x} = \frac{1}{2} N(x) - \frac{1}{2} N(x + \delta x)$$
$$= -\frac{1}{2} [N(x + \delta x) - N(x)]$$

$$J_x = \frac{\text{No. crossing}}{A \tau} = -\frac{1}{2} \left[\frac{N(x + \delta x) - N(x)}{A \tau} \right]$$

multiply by $\delta x^2 / \delta x^2$:

The relationship of the random walk (the microscopic view) to Fick's first law (the macroscopic view).



multiply by $\delta x^2 / \delta x^2$:

$$J_x = -\frac{\delta x^2}{2\tau} \frac{1}{\delta x} \left[\frac{N(x+\delta x)}{A \delta x} - \frac{N(x)}{A \delta x} \right]$$

$$= -D \left[\frac{c(x+\delta x) - c(x)}{\delta x} \right]$$

$$= -D \frac{dc}{dx}$$

$$\frac{dy}{J_x} = \lim_{\delta x \rightarrow 0} \frac{y(x+\delta x) - y(x)}{\delta x}$$

The physical model:

One need only substitute in Fourier's law the words quantity of heat with the words quantity of dissolved body, and the word temperature with density of solution". (A. Fick, 1855; adapted from Agutter et al. (2001), J. Hist. Biol. 33: 71-111)

$$J = -D \frac{dc}{dx}$$

in 1-D.

Fick's 1st Law

So, Fick's **mapping of diffusion** to Fourier's or Ampere's Laws of heat conduction and current flow is correct.

But what kind of force is a concentration gradient?

Now...the thermodynamic basis for diffusion.

The thermodynamic basis for diffusion.

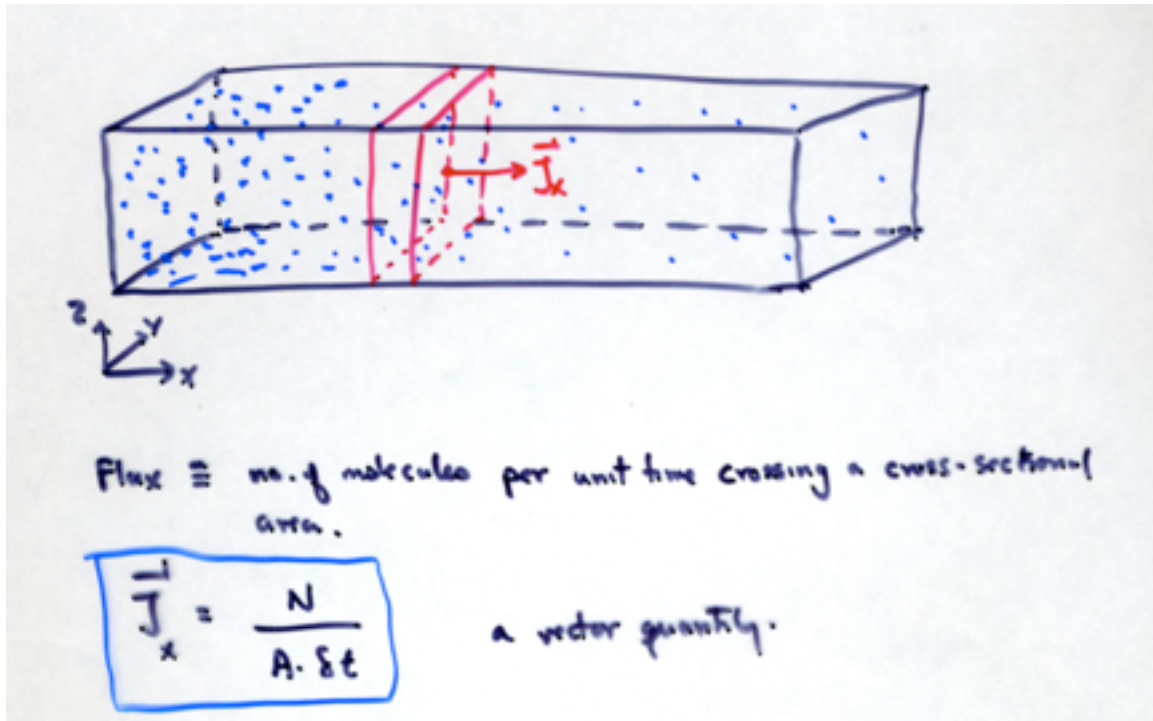
So... Fick's is an empirical relationship.

$$\vec{J}_x = -D \frac{dc}{dx}$$

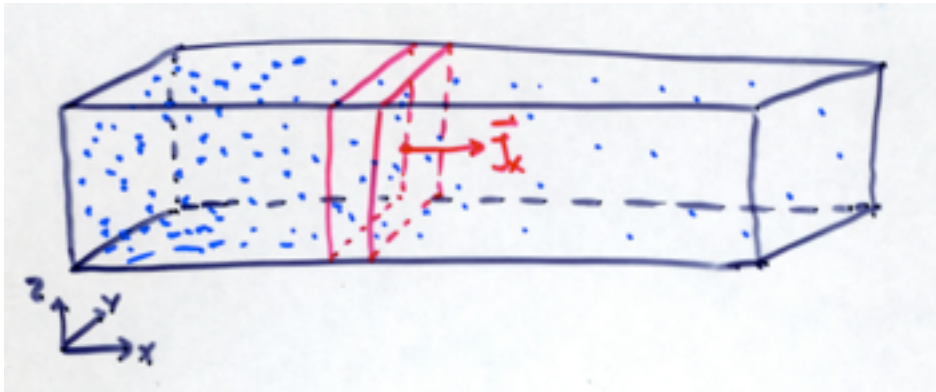
What is a concentration gradient in thermodynamic terms? Well...
it is a gradient of molar free energy.

To understand this, we begin with some definitions
and some review of thermodynamics....

Now...the thermodynamic basis for diffusion.



Now...the thermodynamic basis for diffusion.



Fick's Law :

$$\vec{J}_x = -D \frac{dc}{dx}$$

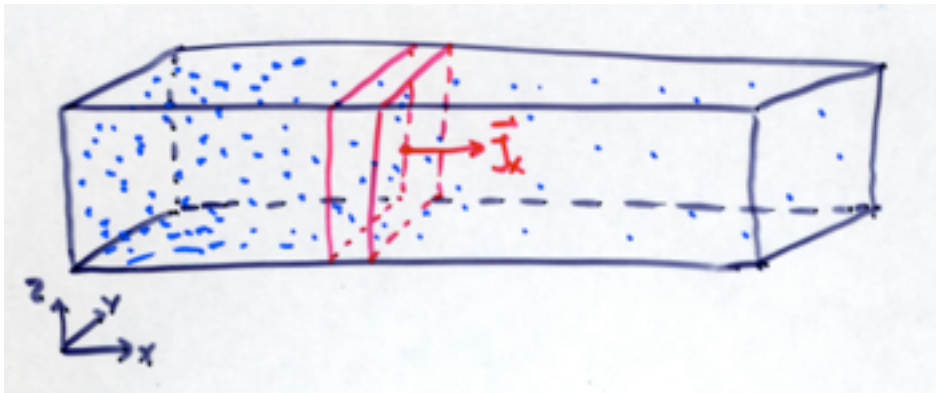
If concentration gradient is in 3-D :

$$\vec{J} = -D \left[i \frac{\partial c}{\partial x} + j \frac{\partial c}{\partial y} + k \frac{\partial c}{\partial z} \right]$$

or...
$$\vec{J} = -D \nabla c$$

where the gradient operator is defined as....

Now...the thermodynamic basis for diffusion.



Fick's Law :

$$\vec{J}_x = -D \frac{dc}{dx}$$

If concentration gradient is in 3-D :

$$\vec{J} = -D \left[i \frac{\partial c}{\partial x} + j \frac{\partial c}{\partial y} + k \frac{\partial c}{\partial z} \right]$$

or...
$$\vec{J} = -D \nabla c$$

$$\nabla = \left[i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} \right] \text{ . the gradient operator}$$

Now....some basic laws of thermodynamics.

A reminder...

$$G = G(T, P, N_1, N_2, \dots, N_i, \dots)$$

free energy is a function of a number of so-called
“natural variables”...

Now....some basic laws of thermodynamics.

A reminder...

$$G = G(T, P, N_1, N_2, \dots, N_i, \dots)$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, N} dP + \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial N_1}\right)_{P, T, N_{i \neq 1}} dN_1 + \left(\frac{\partial G}{\partial N_2}\right)_{P, T, N_{i \neq 2}} dN_2 + \dots$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, N} dP + \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \sum_{i=1}^s \left(\frac{\partial G}{\partial N_i}\right)_{P, T, N_{j \neq i}} dN_i$$

and the derivative of free energy involves taking partial derivatives of the function G with respect to these natural variables...

so what are these partial derivatives? They have key physical interpretations...

Now....some basic laws of thermodynamics.

A reminder...

$$G = G(T, P, N_1, N_2, \dots, N_i, \dots)$$

Now...

$$\left(\frac{\partial G}{\partial P}\right)_{T, N} \equiv V \quad [\text{volume}]$$

$$\left(\frac{\partial G}{\partial T}\right)_{P, N} \equiv -S \quad [\text{entropy}]$$

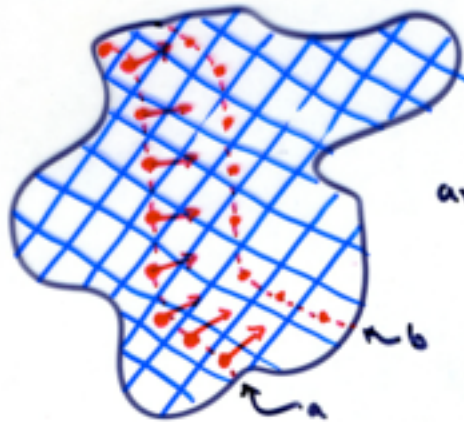
$$\left(\frac{\partial G}{\partial N_i}\right)_{P, T, N_{j \neq i}} \equiv \mu_i \quad [\text{chemical potential}]$$

$$dG = V dP + (-S dT) + \sum_{i=1}^x \mu_i dN_i$$

And so we get the basic definition of infinitesimal changes in Gibbs free energy....the basic equation of equilibrium thermodynamics.

Ok, with this, let's go back to our problem of diffusion....

Consider a thermodynamic system at constant pressure and at thermal equilibrium with surroundings. It has a gradient of chemical potential...



$$\mu \equiv \left. \frac{\partial G}{\partial n} \right|_{T,P}$$

This is a scalar quantity. a and b are isopotential surfaces.

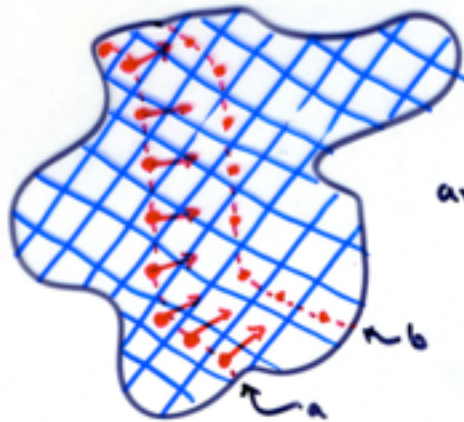
$$\nabla \mu = \vec{i} \frac{\partial \mu}{\partial x} + \vec{j} \frac{\partial \mu}{\partial y} + \vec{k} \frac{\partial \mu}{\partial z}$$

This is a vector field. For isopotential ... ?

Now which way will particles at a move? Along a ? Away from a ? Towards b ?

Ok, with this, let's go back to our problem of diffusion....

Consider a thermodynamic system at constant pressure and at thermal equilibrium with surroundings. It has a gradient of chemical potential...



$$\mu \equiv \left. \frac{\partial G}{\partial n} \right|_{T,P}$$

This is a scalar quantity. a and b are isopotential surfaces.

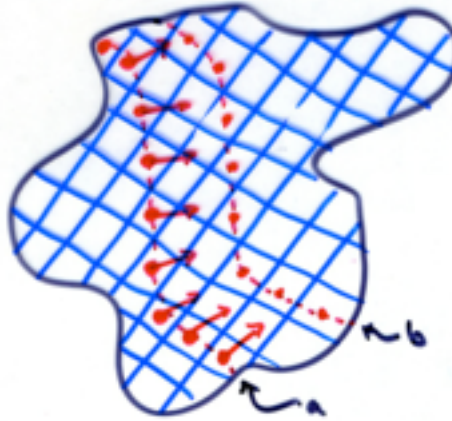
$$\nabla \mu = \vec{i} \frac{\partial \mu}{\partial x} + \vec{j} \frac{\partial \mu}{\partial y} + \vec{k} \frac{\partial \mu}{\partial z}$$

This is a vector field. for isopotential ... ?

Now which way will particles at a move? Along a? Away from a? Towards b?

Well, the direction of spontaneous change is the direction of maximal negative free energy change. So...

Ok, with this, let's go back to our problem of diffusion....

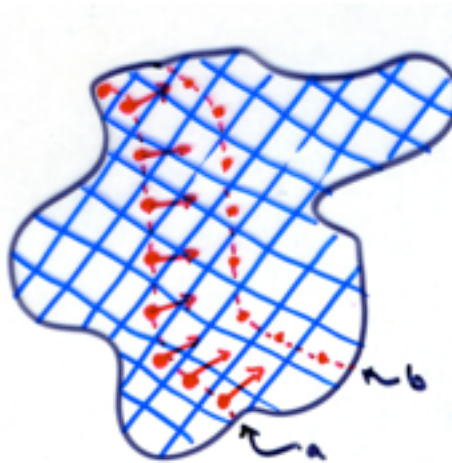


So...

$$\mu = \frac{\partial G}{\partial n} \Big|_{T,P}$$

$$\nabla \mu = \vec{i} \frac{\partial \mu}{\partial x} + \vec{j} \frac{\partial \mu}{\partial y} + \vec{k} \frac{\partial \mu}{\partial z}$$

Ok, with this, let's go back to our problem of diffusion....



So...

$$\mu = \frac{\partial G}{\partial n} \Big|_{T,P}$$

$$\nabla \mu = i \frac{\partial \mu}{\partial x} + j \frac{\partial \mu}{\partial y} + k \frac{\partial \mu}{\partial z}$$

$$= i \left(\frac{\partial}{\partial x} \left(\frac{\partial G}{\partial n} \right) \right) + j \left(\frac{\partial}{\partial y} \left(\frac{\partial G}{\partial n} \right) \right) + k \left(\frac{\partial}{\partial z} \left(\frac{\partial G}{\partial n} \right) \right)$$

$$= i \left(\frac{\partial}{\partial n} \left(\frac{\partial G}{\partial x} \right) \right) + j \left(\frac{\partial}{\partial n} \left(\frac{\partial G}{\partial y} \right) \right) + k \left(\frac{\partial}{\partial n} \left(\frac{\partial G}{\partial z} \right) \right)$$

Ok, with this, let's go back to our problem of diffusion....



So...

$$\mu = \left. \frac{\partial G}{\partial n} \right|_{T,P}$$

$$\nabla \mu = \vec{i} \frac{\partial \mu}{\partial x} + \vec{j} \frac{\partial \mu}{\partial y} + \vec{k} \frac{\partial \mu}{\partial z}$$

$$= \vec{i} \left(\frac{\partial}{\partial x} \left(\frac{\partial G}{\partial n} \right) \right) + \vec{j} \left(\frac{\partial}{\partial y} \left(\frac{\partial G}{\partial n} \right) \right) + \vec{k} \left(\frac{\partial}{\partial z} \left(\frac{\partial G}{\partial n} \right) \right)$$

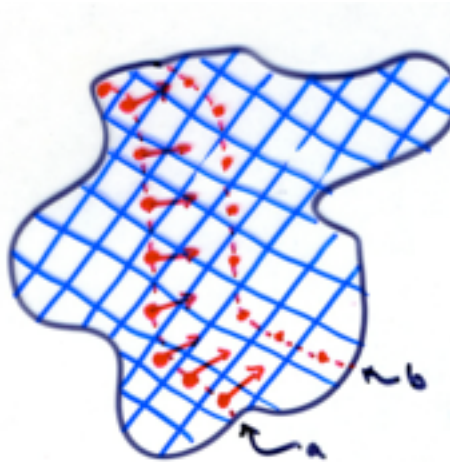
$$= \vec{i} \left(\frac{\partial}{\partial n} \left(\frac{\partial G}{\partial x} \right) \right) + \vec{j} \left(\frac{\partial}{\partial n} \left(\frac{\partial G}{\partial y} \right) \right) + \vec{k} \left(\frac{\partial}{\partial n} \left(\frac{\partial G}{\partial z} \right) \right)$$

So...

① for $\nabla \mu \neq 0$, there must be a non-zero spatial gradient of free energy.

② If $\nabla \mu = 0$ (isopotential surface), and $\mu \neq 0$ then all spatial gradients of free energy must be 0.

Ok, with this, let's go back to our problem of diffusion....



Thus...

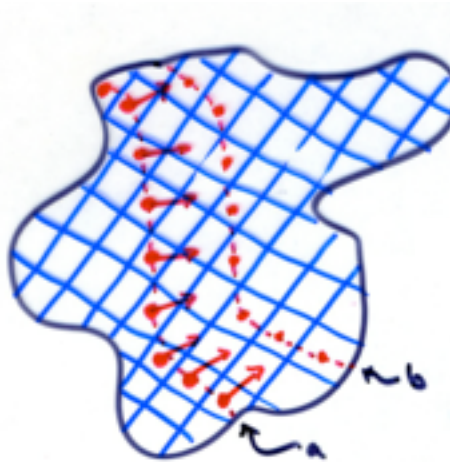
- ① No net flux on isopotential surfaces.
- ② ~~Direction~~ Net flux is non-zero if there are spatial gradients of free energy.
- ③ flux is maximal along directions of maximal negative free energy.

$$\vec{J} \propto -\nabla\mu$$

The gradient of chemical potential is the "force" for diffusion.

....and **one more step** get's us to back to Fick's law....

Ok, with this, let's go back to our problem of diffusion....



$$\mu = \mu^0 + kT \ln C \quad , \text{ where } C \text{ is concentration.}$$

$$\nabla \mu = \frac{kT}{C} \nabla C \quad , \text{ because } \boxed{\frac{d \ln y}{dx} = \frac{1}{y} \frac{dy}{dx}}$$

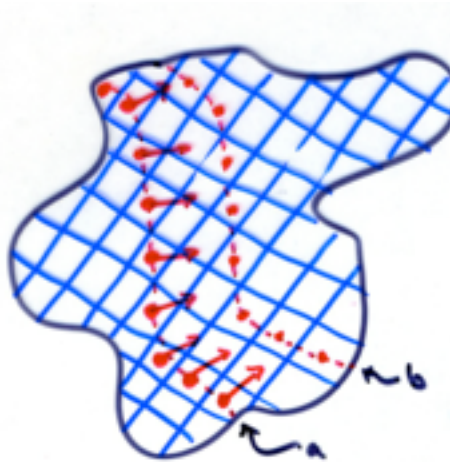
So...

$$\boxed{\vec{J} = - \frac{\alpha kT}{C} \nabla C}$$

This is fick'e law with $D = \frac{\alpha kT}{C}$

One important point here....

Ok, with this, let's go back to our problem of diffusion....

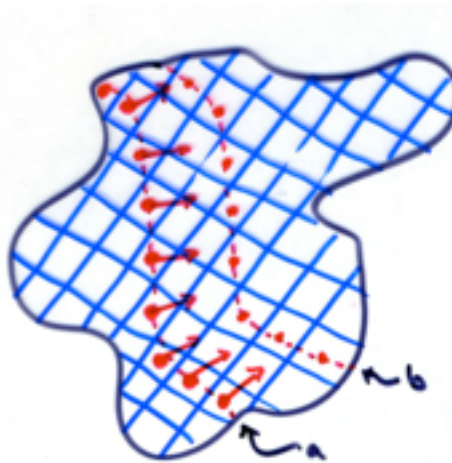


New another point.

$$\begin{aligned}\mu &= \left. \frac{\partial G}{\partial n} \right|_{T,P} \\ &= \left. \frac{\partial H}{\partial n} \right|_{T,P} - T \left. \frac{\partial S}{\partial n} \right|_{T,P}\end{aligned}$$

For an ideal dilute solution, what are the enthalpic contributions to the chemical potential?

Ok, with this, let's go back to our problem of diffusion....



Now another point.

$$\begin{aligned}\mu &= \left. \frac{\partial G}{\partial n} \right|_{T,P} \\ &= \left. \frac{\partial H}{\partial n} \right|_{T,P} - T \left. \frac{\partial S}{\partial n} \right|_{T,P}\end{aligned}$$

For an ideal dilute solution, what are the enthalpic contributions to the chemical potential?

So ... the essence of the chemical potential gradient (or concentration gradient) is the molar entropy gradient. The flow of particles down a concentration gradient is the consequence of a system seeking a condition of maximum entropy.

Fick's Second Law....The Diffusion Equation

The first law gives us flux as a function of concentration gradient :

$$\vec{j}_x = -D \frac{dc}{dx}$$

or $\vec{j} = -D \nabla C$ where ∇ is the gradient operator

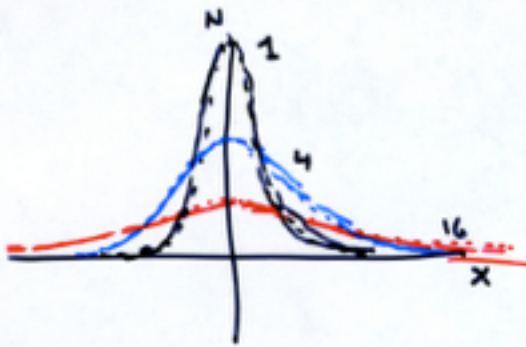
Fick's Second Law....The Diffusion Equation

The first law gives us flux as a function of concentration gradient :

$$\vec{j}_x = -D \frac{dc}{dx}$$

or $\vec{j} = -D \nabla C$ where ∇ is the gradient operator

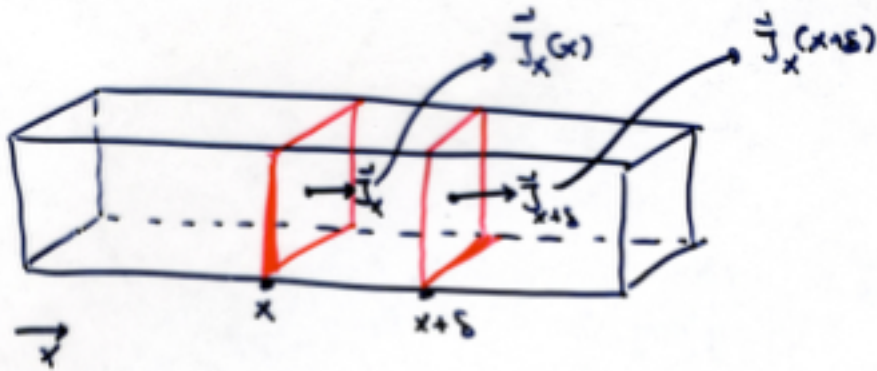
But often, the concentration gradient itself is a function of time as well as space. Remember our example of how the distribution of particles started at one location goes with time ?



→ So, the concentration gradient is collapsing over time.

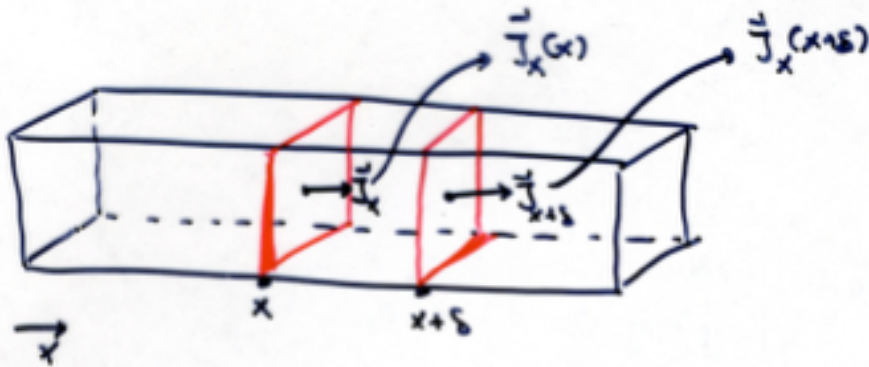
To understand this, we return to our 1D diffusion problem....

Fick's Second Law....The Diffusion Equation



So ... we have slab of (infinitesimal) thickness δ , and we have fluxes \vec{J}_x at x and $\vec{J}_{x+\delta}$ at $x+\delta$. Now these two fluxes need not be equal, but if not

Fick's Second Law....The Diffusion Equation

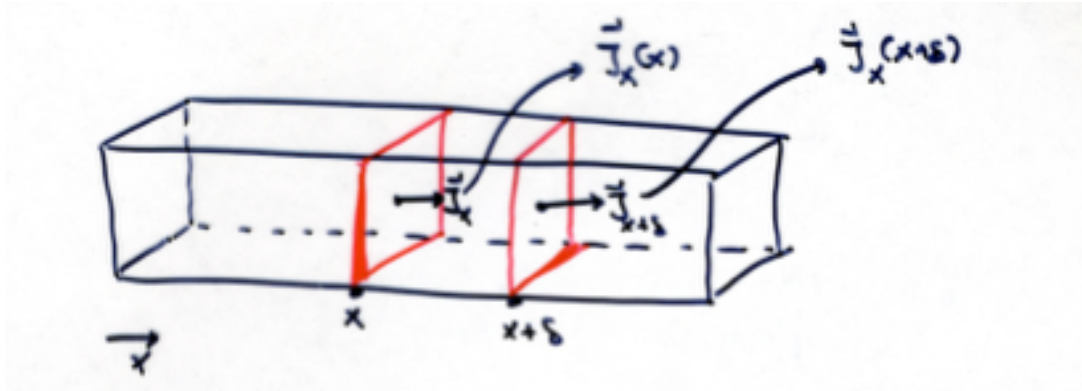


So ... we have slab of (infinitesimal) thickness δ , and we have fluxes \vec{J}_x at x and $\vec{J}_{x+\delta}$ at $x+\delta$. Now these two fluxes need not be equal, but if not ...

then the slab must be gaining or losing particles [conservation of mass]. So we can write down how the concentration in the slab changes over time with regard to the fluxes at the slab boundaries ...

$$\begin{aligned} \text{No. of particles entering in period } \tau &= J_x(x) \cdot A \cdot \tau \\ \text{" " leaving " " } &= J_x(x+\delta) \cdot A \cdot \tau \end{aligned}$$

Fick's Second Law....The Diffusion Equation



$$\begin{aligned} \text{No. of particles entering in period } \tau &= J_x(x) \cdot A \cdot \tau \\ \text{" " leaving " " } &= J_x(x+\delta) \cdot A \cdot \tau \end{aligned}$$

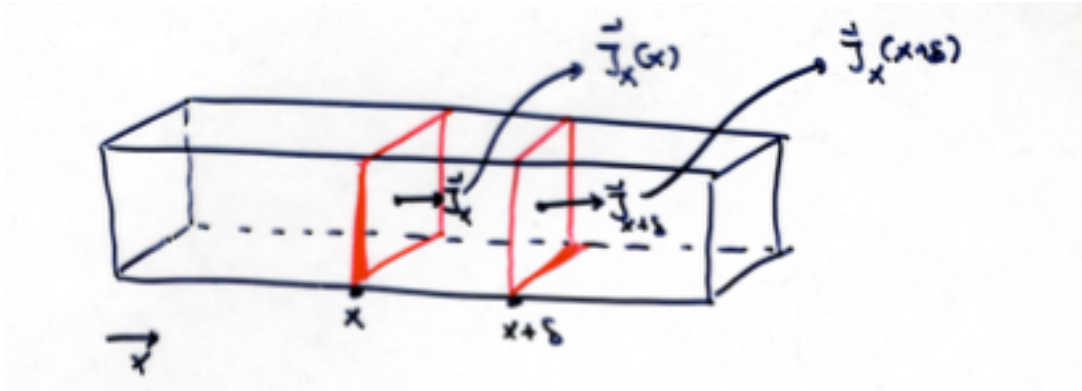
So...

$$\frac{C(t+\tau) - C(t)}{\tau} = \frac{1}{\tau} \left[-\frac{J_x(x+\delta) A \tau}{A \delta} + \frac{J_x(x) A \tau}{A \delta} \right]$$

$$\text{or... } \frac{C(t+\tau) - C(t)}{\tau} = -\frac{J_x(x+\delta) - J_x(x)}{\delta}$$

Taking the limits as both tau and delta approach zero...

Fick's Second Law....The Diffusion Equation



Taking limits as $\tau \rightarrow 0$ and $\delta \rightarrow 0$...

17

$$\lim_{\tau \rightarrow 0} \frac{C(t+\tau) - C(t)}{\tau} = - \lim_{\delta \rightarrow 0} \frac{J_x(x+\delta) - J_x(x)}{\delta}$$

$$\frac{\partial C}{\partial t} = - \frac{\partial J_x}{\partial x}$$

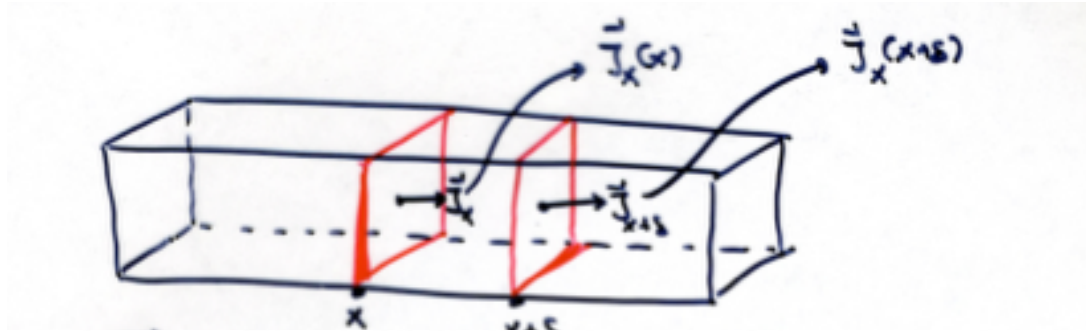
Now Fick's first law says that $J_x = -D \frac{\partial C}{\partial x}$

$$\frac{\partial C}{\partial t} = - \frac{\partial}{\partial x} \left(-D \frac{\partial C}{\partial x} \right)$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Fick's Second Law (in 1-D)

Fick's Second Law....The Diffusion Equation



If we generalize to 3D ...

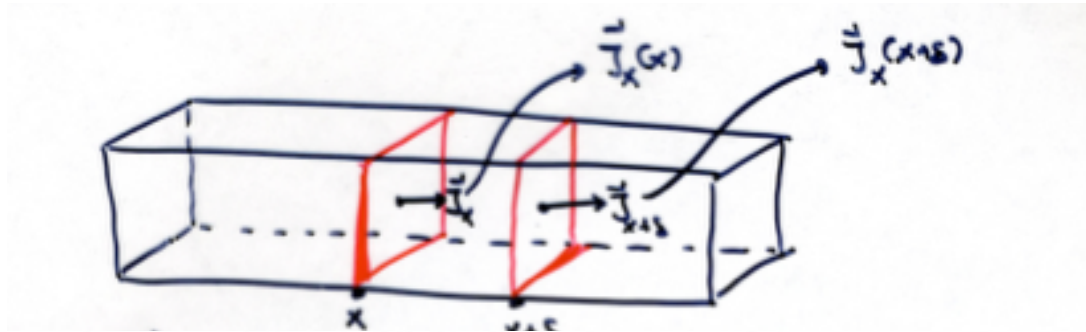
$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} \quad , \quad \text{but since } \mathbf{J} = -D \nabla c$$

$$\boxed{\frac{\partial c}{\partial t} = D \nabla^2 c}$$

Fick's second law, more generally. Also called the diffusion equation

Note: The operator ∇^2 is called the Laplacian and is shorthand for second derivatives in all dimensions ...

Fick's Second Law....The Diffusion Equation



If we generalize to 3D ...

$$\frac{\partial C}{\partial t} = -\nabla \cdot \mathbf{J} \quad , \quad \text{but since } \mathbf{J} = -D \nabla C$$

$$\boxed{\frac{\partial C}{\partial t} = D \nabla^2 C}$$

Fick's Second Law, more generally. Also called the diffusion equation

Note: The operator ∇^2 is called the Laplacian and is shorthand for second derivatives in all dimensions ...

$$\nabla^2 = \left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad , \quad \text{the Laplacian.}$$

Fick's Second Law....The Diffusion Equation

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

Fick Second Law, more generally. Also called the diffusion equation

So ... solving the diffusion eqn for specific boundary conditions gives the concentration of particles as a function of space and time.

So.. in 3D $C(x, y, z, t)$

Fick's Second Law....The Diffusion Equation

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

Fick's Second Law, more generally. Also called the diffusion equation

So ... solving the diffusion eqn for specific boundary conditions gives the concentration of particles as a function of space and time.

So.. in 3D $C(x, y, z, t)$

For example, for the 1D case in which we start with N_0 molecules at $t=0$ and $x=0$...

$$C(x, t) = \frac{N_0}{\sqrt{4\pi Dt}} e^{\left[-\frac{x^2}{4Dt}\right]}$$

Fick's Second Law....The Diffusion Equation

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

Fick's Second Law, more generally. Also called the diffusion equation.

So ... solving the diffusion eqn for specific boundary conditions gives the concentration of particles as a function of space and time.

So.. in 3D $C(x, y, z, t)$

For example, for the 1D case in which we start with N_0 molecules at $t=0$ and $x=0$...

$$C(x, t) = \frac{N_0}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

You should notice that this is the equation of the Gaussian distribution with a mean of 0 and standard deviation $\sqrt{2Dt}$.

Fick's Second Law....The Diffusion Equation

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

Fick's second law, more generally. Also called the diffusion equation.

For example, for the 1D case in which we start with N_0 molecules at $t=0$ and $x=0$...

$$C(x,t) = \frac{N_0}{\sqrt{4\pi Dt}} e^{\left[\frac{-x^2}{4Dt}\right]}$$

Again... ① particles go nowhere on average,

② the spatial distribution is a bell-shaped curve for all times, and

③ the spread of molecules goes as the square root of time.

Fick's Second Law....The Diffusion Equation

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

Fick's second law, more generally. Also called the diffusion equation

For example, for the 1D case in which we start with N_0 molecules at $t=0$ and $x=0$...

$$C(x,t) = \frac{N_0}{\sqrt{4\pi Dt}} e^{\left[\frac{-x^2}{4Dt}\right]}$$

Again... ① particles go nowhere on average,

② the spatial distribution is a bell-shaped curve for all times, and

③ the spread of molecules goes as the square root of time.

→ So... $D_{\text{max}} (D = 1.19 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ in H}_2\text{O})$ can move 15 μm in 1 sec but takes 1 hour to go 1mm and takes 1yr to move 9 mm!!

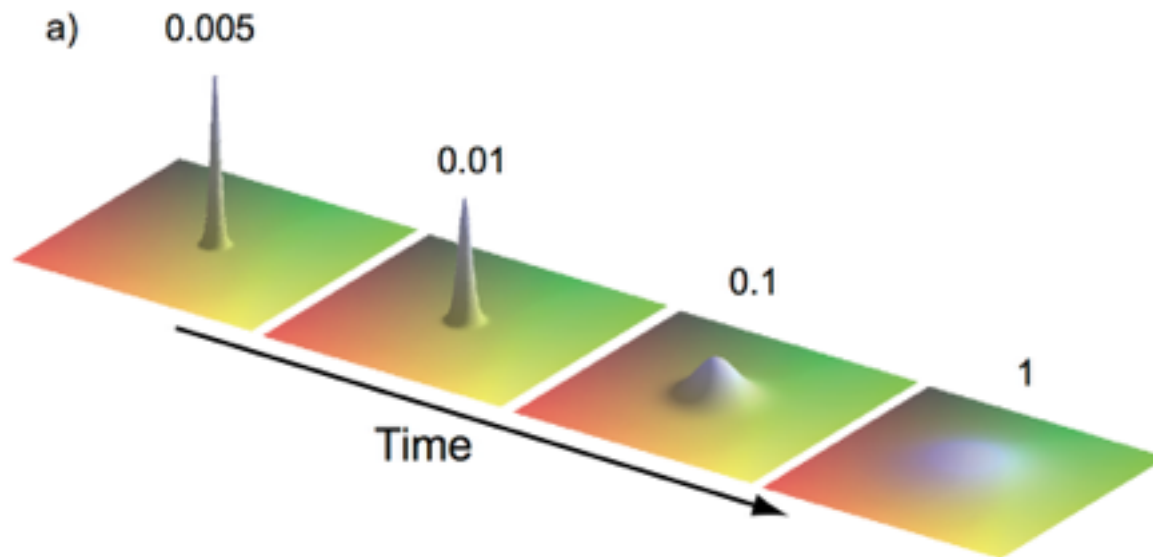
Diffusion is slow over long distances ...

Fick's Second Law....The Diffusion Equation

$$\frac{\partial C}{\partial t} = D \nabla^2 C$$

Fick's second law, more generally. Also called the diffusion equation.

One can solve higher dimensional versions of the diffusion equation...in general many complex phenomena can be explained by solutions to this equation.



Next time...the theory of diffraction

	$n = 1$	$n = 2$ or 3	$n \gg 1$	continuum
Linear	exponential growth and decay	second order reaction kinetics	electrical circuits	Diffusion
	single step conformational change	linear harmonic oscillators	molecular dynamics	Wave propagation
	fluorescence emission	simple feedback control	systems of coupled harmonic oscillators	quantum mechanics
	pseudo first order kinetics	sequences of conformational change	equilibrium thermodynamics	viscoelastic systems
Nonlinear	fixed points	anharmonic oscillators	systems of non-linear oscillators	Nonlinear wave propagation
	bifurcations, multi stability	relaxation oscillations	non-equilibrium thermodynamics	Reaction-diffusion in dissipative systems
	irreversible hysteresis	predator-prey models	protein structure/function	Turbulent/chaotic flows
	overdamped oscillators	van der Pol systems	neural networks	
		Chaotic systems	the cell	
			ecosystems	