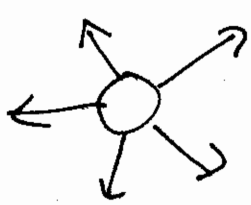
Phys 347 Topic 3

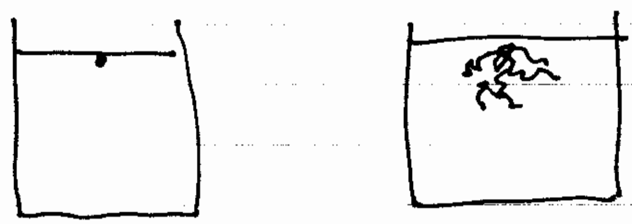
Diffusion:

Motivation:

- previously we learned that temperature was related to the average kinetic energy of a particle
- this thermal (random) motion has an energy $\frac{1}{2} k_B T$ for each spatial direction
- Friction is nothing more than the turning of ordered motion into disordered (thermal) motion $\equiv$ dissipative process
- for small molecules the thermal energy due to random kicks from other molecules is NOT small $\Longrightarrow$ leads to molecule performing a random walk. $\equiv$ Brownian motion



ink in water:

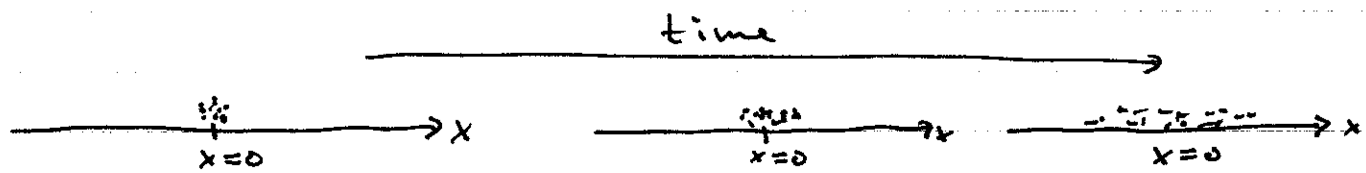


- ink diffuses in water $\equiv$ random walk of ink molecules.

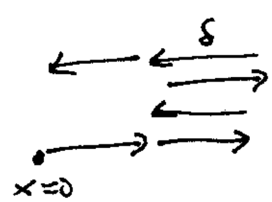
- Diffusion is the main means of transport in the cell
- Diffusion is described by the mathematics of random walks — has broader applications (polymer physics, spin physics)

Random Walks:

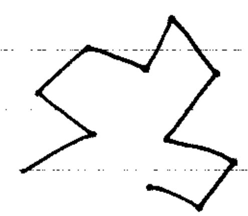
- Consider N particles, each moving with an average speed $v_x = \sqrt{kT/m}$
- How do they spread in time?



- If we look @ one molecule's walk:



or in 2D



① On average it collides every Δt seconds, and during this time has moved $\delta = \pm v_x \Delta t$.
② The $\pm$ simply expresses that it moves with equal probability to the left and right.
③ Particles are independent – motion doesn't depend on the others

- Calculate $\langle x \rangle$ and $\langle x^2 \rangle$ over all N particles:

$\langle x \rangle$:

- let $x_i(n) \equiv$ position of ith particle after n steps.

$$x_i(n) = x_i(n-1) \pm \delta \qquad \text{(50% moves left/right)}$$

so

$$\langle x(n) \rangle = \frac{1}{N} \sum_{i=1}^{N} x_i(n)$$

$$= \frac{1}{N} \sum_{i=1}^{N} (x_i(n-1) \pm \delta) = \frac{1}{N} \sum_{i=1}^{N} x_i(n-1) + \cancelto{0}{\frac{1}{N} \sum_{i=1}^{N} \pm \delta}$$

$$= \langle x(n-1) \rangle$$

so

if $\langle x(0) \rangle = 0$ then $\langle x(n) \rangle = 0$ for all time

$\Rightarrow$ on average there is no net drift of the particles from $x=0$ – they remain centred.

$\langle x^2 \rangle$:

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

$$= \frac{1}{N} \sum_{i=1}^{N} (x(n-1)^2 \pm \cancelto{0}{2\delta x(n-1)} + \delta^2)$$

so

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

Start with: $\langle x(0)^2 \rangle = 0 \Rightarrow \langle x(1)^2 \rangle = \delta^2$

$$\Rightarrow \langle x(2)^2 \rangle = \langle x(1)^2 \rangle + \delta^2 = 2\delta^2 \quad \text{etc....}$$

so $$\langle x(n)^2 \rangle = n\,\delta^2$$

but, & total time, $t = n\Delta t$ so $n = t/\Delta t$

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

rewrite: $$\boxed{\langle x^2(t) \rangle = 2Dt}$$

where
$$D = \frac{1}{2}\frac{\delta^2}{\Delta t} = \frac{1}{2} v_x^2 \Delta t$$

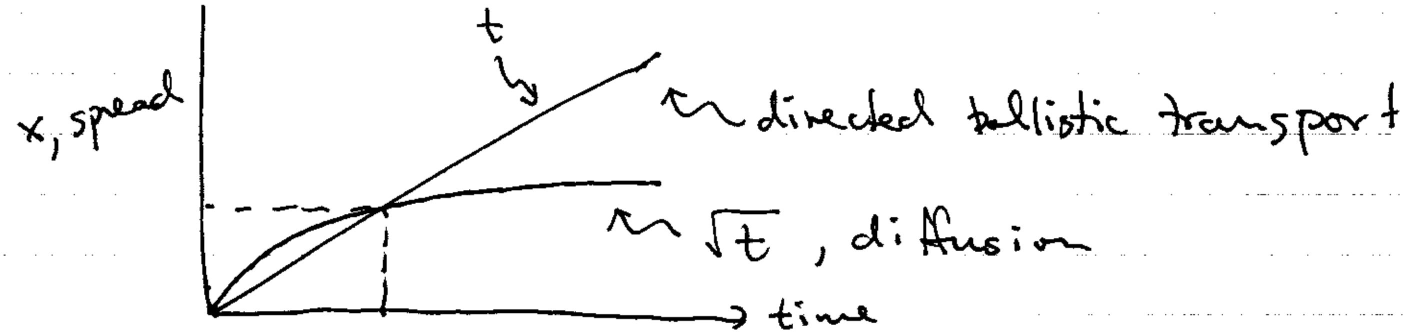
$\equiv$ Diffusion coefficient $[m^2/t]$

3D: $$\boxed{\langle \vec{r}^{\,2}(t) \rangle = 6Dt}$$

2D: $$\boxed{\langle \vec{r}^{\,2}(t) \rangle = 4Dt}$$

So the particles spread in time & this is characterized by the diffusion coeff D.

- This spread only grows as $\sqrt{t}$, whereas a particle moving ballistically, $x \sim v_x t$



- For small distances, diffussion can actually move you faster than ballistic transport.

Some #'s: for small molecule in H_2O, $D \sim 10^{-5} cm^2/s$

- time to traverse the length of a bacteria – $x = 10^{-4} cm$

so $t = \frac{\langle x^2 \rangle}{2D} = 5 \times 10^{-4} s$ ~ milliseconds

$\Rightarrow$ molecules are very well mixed in a bacteria

- time to move 1 cm in a ~~[illegible]~~ neuron:

$t = \frac{\langle x^2 \rangle}{2D} = 5 \times 10^4 s \sim 14$ hours!

neurons use "active" transport = molecular motors

- Most scents reach our nose because there are convective currents – if it were diffusion it would take months to cross a room.

Distribution of positions:

Showed $\langle x(t) \rangle = 0$ & $\langle x^2(t) \rangle = 2Dt$

what about the probability distribution of x? $P(x,t)$

Binomial dist'n:

- Consider a particle can move to the right with probability p, the prob of moving left is $q = 1-p$.
- Particle makes n moves, k are to the right. say it's, r r l r l . . . l r , k r's.

$$\text{Prob} = p^k q^{n-k}$$

- Prob of k moves to the right → there are $\frac{n!}{k!(n-k)!}$ sequences that have k moves to the right.

so

$$P(k) = \frac{n!}{k!(n-k)!} p^k q^{n-k} \equiv \text{binomial dist'n}$$

Now: $x(n) = k\delta - (n-k)\delta = (2k-n)\delta$

so $\langle x(n) \rangle = (2\langle k \rangle - n)\delta$

where $\langle k \rangle = np$ for binomial

if $p = 1/2 \Rightarrow \langle x(n) \rangle = 0$

and

$$\langle x^2(n)\rangle = \langle [(2k-n)\delta]^2\rangle = (4\langle k^2\rangle - 4\langle k\rangle n + n^2)\delta^2$$

$$\& \quad \langle k^2\rangle = (np)^2 + npq$$

again for $p = 1/2$, $\langle x^2(n)\rangle = n\delta^2$

Now for diffusing particles, n & np are large! In one second, a particle will take about $\underline{\underline{10^{12}}}$ steps.

- When n & np are large, the binomial distribution becomes a gaussian, so

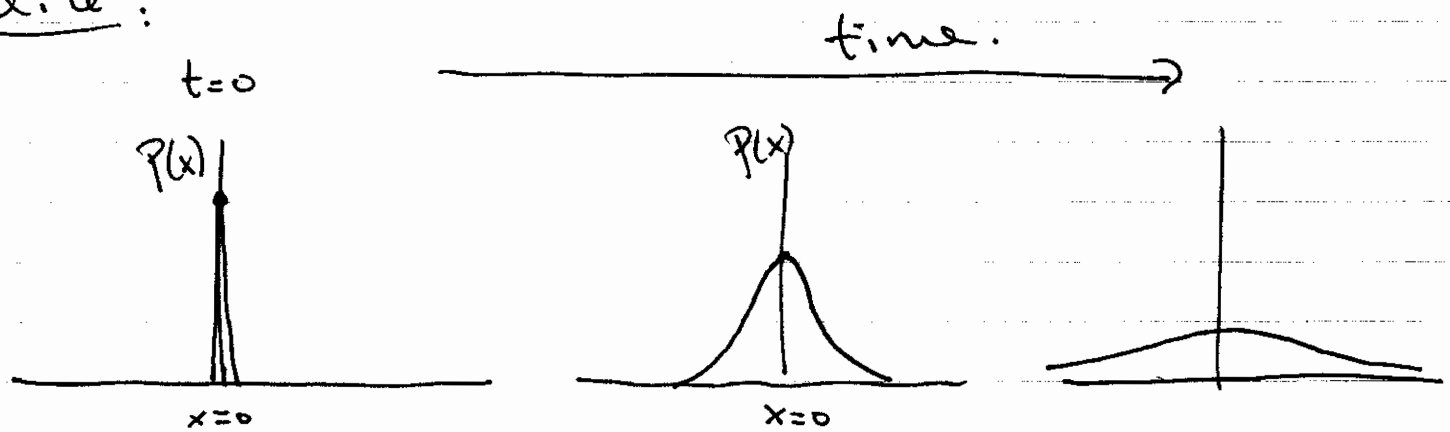
$$P(k)\,dk = \frac{1}{(2\pi\sigma^2)^{1/2}} e^{-(k-\mu)^2/2\sigma^2} dk$$

where $\mu = np = \langle k\rangle$ & $\sigma = npq = \langle k^2\rangle - \langle k\rangle^2$

Converting this to spatial (assignment):

$$\boxed{P(x)\,dx = \frac{1}{(4\pi Dt)^{1/2}} e^{-x^2/4Dt}\,dx}$$

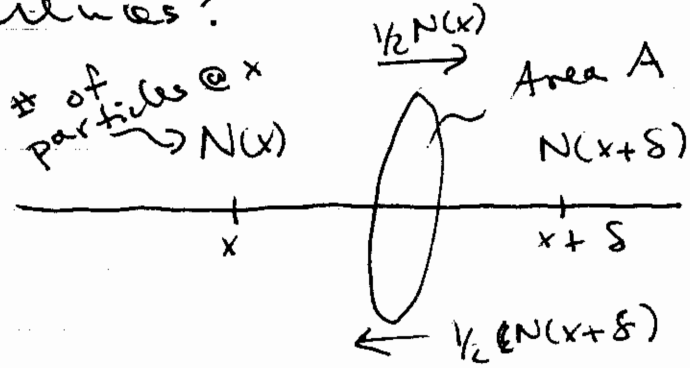
Visualize:



What about macroscopic difusive transport? Osmosis etc.?

Fick's Law:

What is the flux of particles due to concentration differences?



@ $t+\Delta t$: $\frac{1}{2}N(x)$ move right across A

$\frac{1}{2}N(x-\delta)$ move left across A

. Net flow: $\frac{1}{2}N(x) - \frac{1}{2}N(x+\delta)$

Define flux: $j = -\frac{1}{2}\left[\frac{N(x+\delta) - N(x)}{A\,\Delta t}\right] = \#/\text{second}/\text{area}$

$\times(\delta^2/\delta^2)$:

$$j = -\underbrace{\left(\frac{\delta^2}{2\Delta t}\right)}_{D}\frac{1}{\delta}\left[\underbrace{\frac{N(x+\delta)}{A\delta}}_{C(x+\delta)} - \underbrace{\frac{N(x)}{A\delta}}_{C(x)}\right] \quad \text{concentrations}$$

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

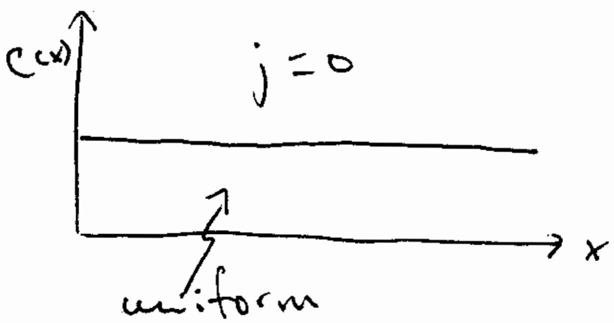
$$j = -D\frac{dC(x)}{dx}$$

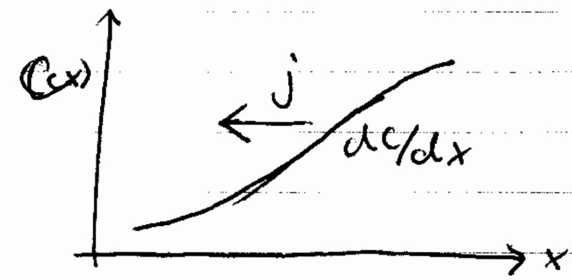
So:

$$\boxed{j = -D\,\frac{dC(x)}{dx}}$$

Thus: if there is a concentration gradient there will be a flux of particles.

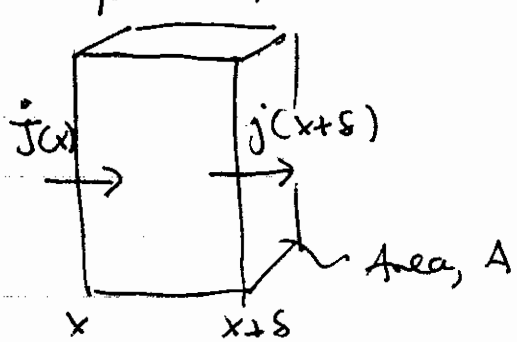
e.g.





- Particles diffuse from regions of high concentration to Low. There is <u>NO</u> external force. Particles are getting pushed by probability — more particles = greater chance to move in one direction. → entropic force.

Consider the # of particles entering/leaving a box over time Δt. There are $j(x)\cdot A\cdot \Delta t$ entering & $j(x+\delta)A\cdot\Delta t$ leaving.



Concentration change:

$$\frac{C(t+\Delta t) - C(t)}{\Delta t}$$

$$= -\frac{1}{\cancel{\Delta t}}\left[j(x+\delta) - j(x)\right]\frac{\cancel{A\Delta t}}{\cancel{A}\delta}$$

So as Δt & $\delta \to 0$

$$\frac{C(t+\Delta t) - C(t)}{\Delta t} = \frac{dC}{dt} = -\left[\frac{j(x+\delta) - j(x)}{\delta}\right] = -\frac{dj}{dx}$$

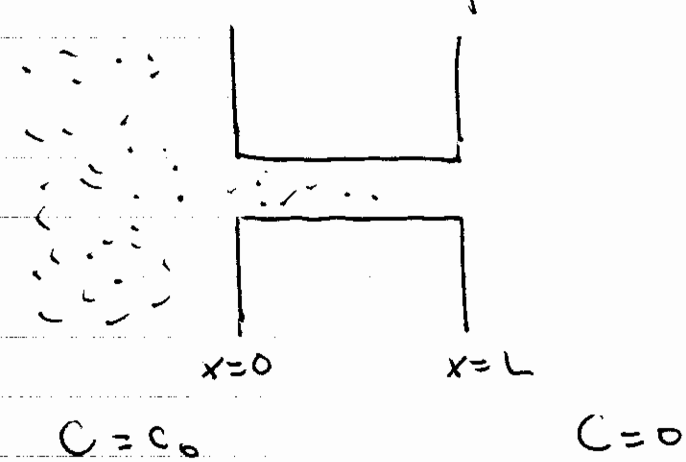
using Fick's Law:

$$\boxed{\frac{dc}{dt} = -D\frac{d^2c}{dx^2}} \equiv \text{Diffusion equation.}$$

This is a partial differential equation which in practice is very hard to solve. Therefore we will just take solutions as given. It tells us how the concentration of particles will change in space & time.

Solutions & Applications:

Diffusion through pore:



- Salt diffusing through pore. One side @ concentration C_0 & the other @ $C=0$.

What is $C(x)$?

- Eventually (after a real long time) both sides would reach the same concentration.

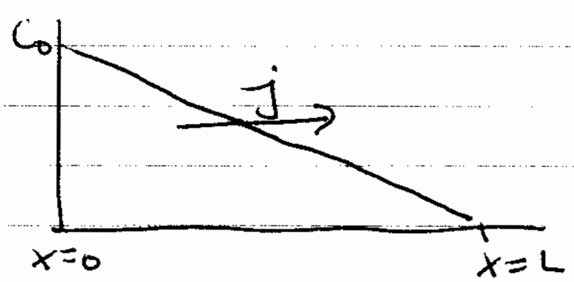
- However @ intermediate times, the system comes to quasi-equilibrium where $c(x)$ doesn't change with time so $dc/dt = 0$.

$$\text{So} \Rightarrow \frac{d^2c}{dx^2} = 0$$

- What function has zero curvature and begins @ $C(0) = C_0$ & ends @ $C(L) = 0$?

- Ans: A line from C_0 to 0 @ $x = L$

$$\text{so} \quad C(x) = C_0\left(1 - \frac{x}{L}\right)$$



flux: $j = -D\dfrac{dc}{dx}$

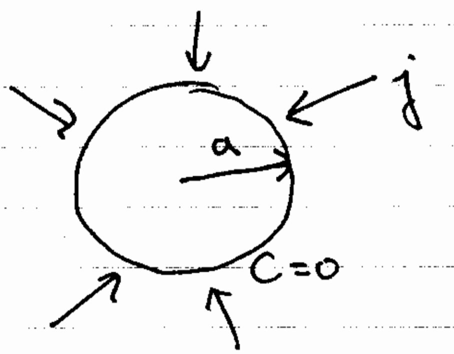
$$j = \frac{DC_0}{L}$$

#'s: $C_0 = 1\,nM = \dfrac{(1\times10^{-9})(6.02\times10^{23})}{1000\ cm^3} = 6.02\times10^{11}/cm^3$

$$D = 10^{-5}\ cm^2/s \quad ; \quad L = 100\,nm = 1\times10^{-5}\ cm$$

$$\text{so} \quad j = \left(\frac{6.02\times10^{11}}{\cancel{cm^3}}\right)\left(\frac{\cancel{10^{-5}}\ \cancel{cm^2}}{s}\right)\left(\frac{1}{\cancel{1\times10^{-5}}\ cm}\right) = 6\times10^{11}/cm^2/s$$

What about a circular cell absorbing nutrients?



$C = C_0$
@ $r = \infty$

Solution: $C(r) = C_0\left(1 - \frac{a}{r}\right)$

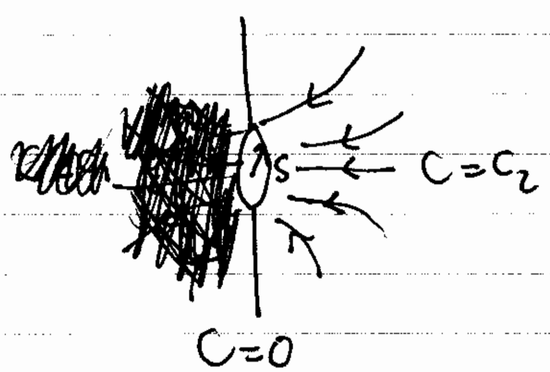
$$j(r) = -DC_0 \frac{a}{r^2}$$

so
net inward current: $I = 4\pi a^2 \, j(a)$

$$I = 4\pi D a C_0$$

N.B.: current only goes as the radius, a, and not as the area a^2

What about a dish-like receptor on a surface?

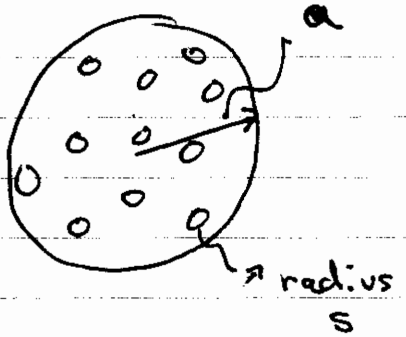


Hard math:

$$I = 4DsC_0$$

again, current goes just as the radius.

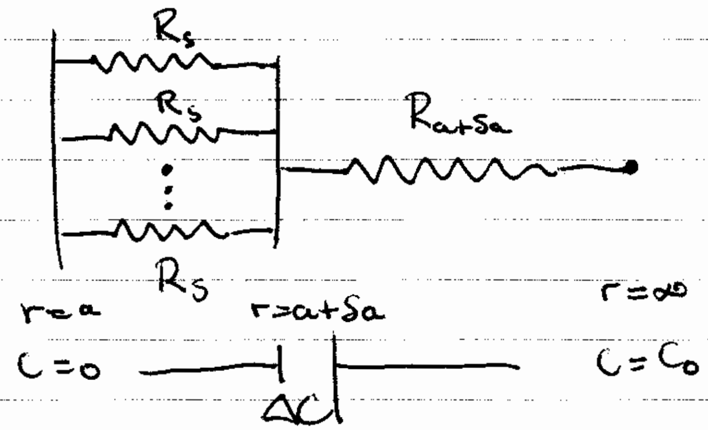
What about N receptors on a cell surface?



$C = C_0$
@ $r = \infty$

- For small N: $I = N(4DsC_0)$
- For large N (cell is completely covered): $I = 4\pi D a C_0$
- What happens in between? for intermediate N?

Coupled resistors: $I = \Delta C / R$, $R \equiv$ resistance



$$R_a = \frac{1}{4\pi D a}$$

$$R_s = \frac{1}{4Ds}$$

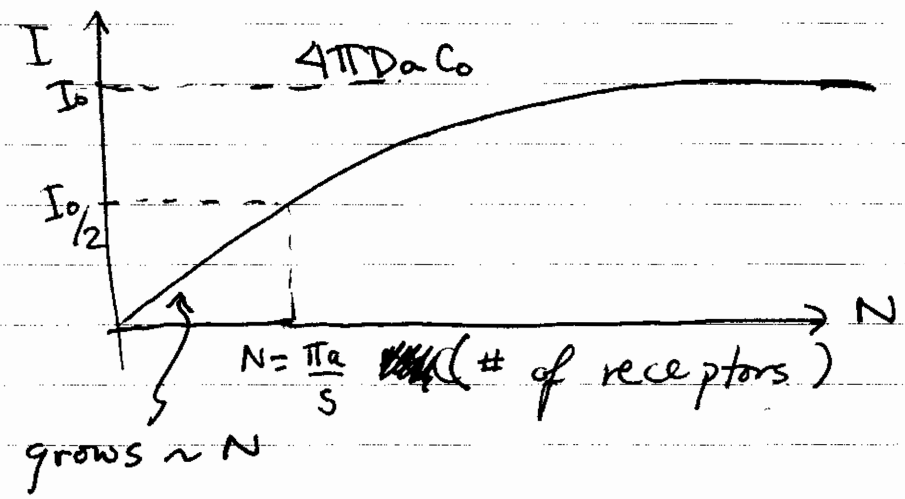
- Total resistance: $R = R_{a+\delta a} + \dfrac{R_s}{N} = \dfrac{1}{4\pi D(a+\delta a)} + \dfrac{1}{4NDs}$
- since $\delta a \ll a$:

$$R \cong \frac{1}{4\pi D a} + \frac{1}{4NDs} = \frac{1}{4\pi D a}\left(1 + \frac{\pi a}{Ns}\right)$$

so

$$I = \frac{\Delta C}{R} = \frac{4\pi D a C_0}{\left(1 + \frac{\pi a}{N s}\right)}$$

Plotting:



- has correct limits: for small N: $I \sim 4NDsC_0$

  for large N: $I \sim 4\pi D a C_0$

#'s: Cell: $a = 5\,\mu m$; $s = 10\,\text{Å}$

N such that $I = \frac{I_0}{2} \rightarrow N = \frac{\pi a}{s}$

so

$$N = (3.14)\frac{(5 \times 10^{-6})}{(10 \times 10^{-10})} = 15\,700 \text{ receptors}$$

~~distance between receptors~~ $\cancel{\sim \left(\frac{4\pi a^2}{N}\right)^{1/2}}$

- amount of surface covered? $\frac{N\pi s^2}{4\pi a^2} \sim 1 \times 10^{-4}$

  $\therefore$ there's lots of room on the surface.