LECTURE 29: CHEMICAL REACTIONS AND DIFFUSIONS

There's a saying in German that says: Everything has an end, except for a sausage, which has two. And with this, I would like to welcome you to the last lecture of our PDE adventure!

Today we'll do something really fun: I'm going to tell you about my PhD research.

One of the perks of PDEs is that not only they are mathematically interesting, but they also model real life phenomena. And in fact, today we're going to explore an equation (or a set of equations) that model chemical reactions. And no worries, you don't need to know any chemistry to do this, the only prereq for this is Breaking Bad :)

I- THE GREAT DEBATE

Consider a very simple chemical reaction $A \rightleftarrows B$, where a molecule A transforms into B and vice-versa. Think for instance of a molecule or a protein that folds (or unfolds) to become another molecule.
(Take note: We are NOT studying $C + O_2 = CO_2$, this is already too complicated)

Then there are two ways of viewing this reaction:

A) MACROSCOPIC LEVEL

On the one hand, on the macroscopic level, you can simply say that there are only the molecules A and B, and you can look at their concentrations:

$a = a(t)$ = concentration of A at time t
$\beta = \beta(t)$ = concentration of B at time t

Then a and β satisfy the following differential equation, called the reaction-diffusion system:

$$\begin{cases} a_t = k\,(\beta - a) \qquad \text{(R-D)} \\ \beta_t = k\,(a - \beta) \end{cases}$$

Here a_t and β_t are the time derivatives of alpha and beta, and $k > 0$ is a positive constant, called the reaction-rate constant (and it's a BIG deal in chemistry to figure out what k is)
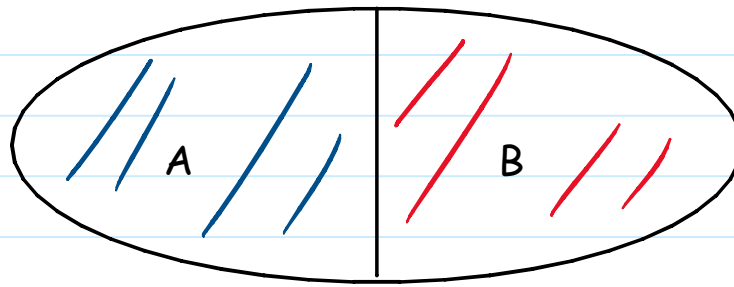
Intuitively, this says: If there are more A-molecules than B-molecules, like in the following picture:
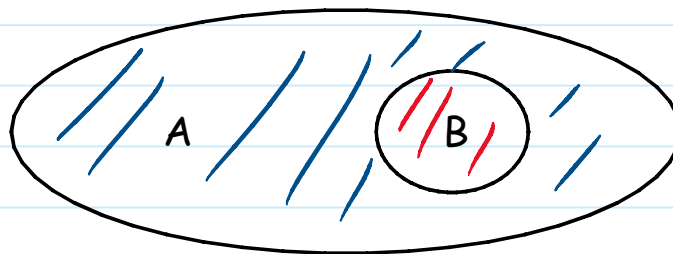
Then $a > \beta$, so $a_t = k(\beta - a) < 0$, so a decreases, so A decreases

On the other hand, $\beta_t = k(a - \beta) > 0$, so B increases

And so this equation says that there is a constant interplay between A and B, until at some point you have equilibrium:

On the other hand, on the microscopic level, instead of just having 2 states A and B, you can actually think of the molecule as having a continuum of states (think of a string), where on the left you have A and on the right you have B, with infinitely many hybrid states in between
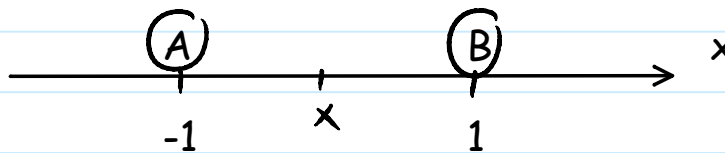

We can parametrize those states with a new variable x, where $x = -1$ is A and $x = 1$ is B. Think of x as a chemical position.

(taking again the protein unfolding-analogy, think of x as the angle of twist)

What's nice about this interpretation is that now we can give a probabilistic flavor of chemical reactions (since reactions are random anyway!):

Namely, you can now think of a molecule as a marble that swings back and forth on a double-well potential function H
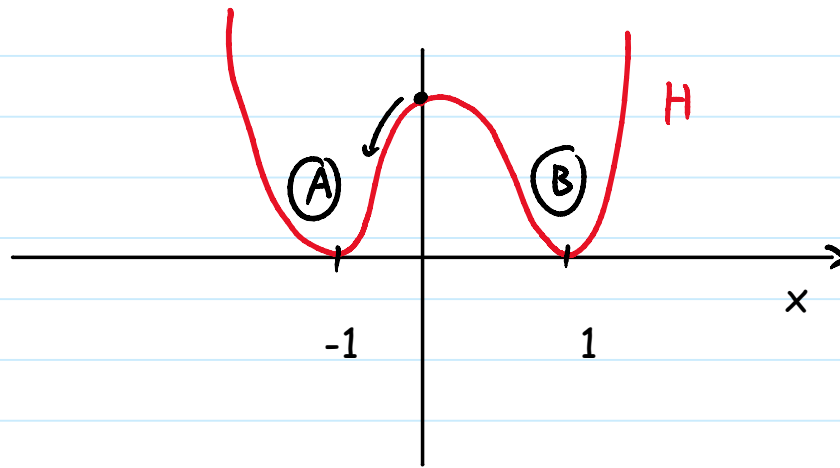
Then the two wells of H correspond to the states A and B, and a chemical reaction corresponds to the passage form A to B

On the potential, this marble performs brownian motion, and in particular we can model its behavior using a PDE called the Kramers-Smoluchowski equation

$$\sigma\, u_t = \left(\frac{\sigma}{\tau}\, u_x \right)_x \qquad \text{(K-S)}$$

Here:

1) $u = u(x,t)$ is the density function of the particle (think probability density function)

2) ε = Zooming factor
   ($\varepsilon = 0$ is the macroscopic state, and $\varepsilon > 0$ is the microscopic state)
   (Everything here depends on ε)

3) $\sigma = \sigma(x) = C\, e^{-H(x)/\varepsilon}$
   (Think of it as H, but we scale it by ε to make it HARD to go from A to B :)

$\frac{H}{\epsilon}$
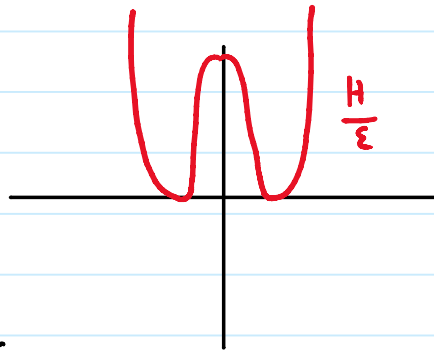
C is such that $\int \sigma = 1$, just like for the heat equation

4) τ = Some constant that makes this work
(Think of it as the speed of the reaction: If τ is too small, then the reaction is too slow and you get 0; if τ is too large, then the reaction is too fast and you get instantaneous equilibrium)

It looks like a mysterious equation, but notice that if you ignore σ and σ/τ, then you get $u_t = u_{xx}$, which is the heat equation! So it's just a scaled version of the heat equation

Those two models stirred a GREAT debate in the chemical world, because some chemists say that the macroscopic model is better, while others say the microscopic one is more accurate.

What I'm claiming is that there shouldn't be a debate at all because it turns out that the two models are just different sides of the same coin!

II- MAIN RESULT

Namely, it turns out that if you take the limit of (K-S) as ϵ goes to 0, you get the (R-D) system!

WHAT???? How are the two equations *possibly* related? In (K-S) you have 1 function u that depends on x and t, where in (R-D) you have 2 functions α and β that only depend on t

What saves us here is... ANALYSIS (in particular something called functional analysis). More precisely, there is a very nice kind of convergence called weak-* convergence that is very suited for this kind of result:

MAIN THEOREM:

1) $\sigma(x)\, u(x,t) \;\rightarrow\; \alpha(t)\, \delta_{\{x=-1\}} + \beta(t)\, \delta_{\{x=1\}}$ as $\varepsilon \rightarrow 0$
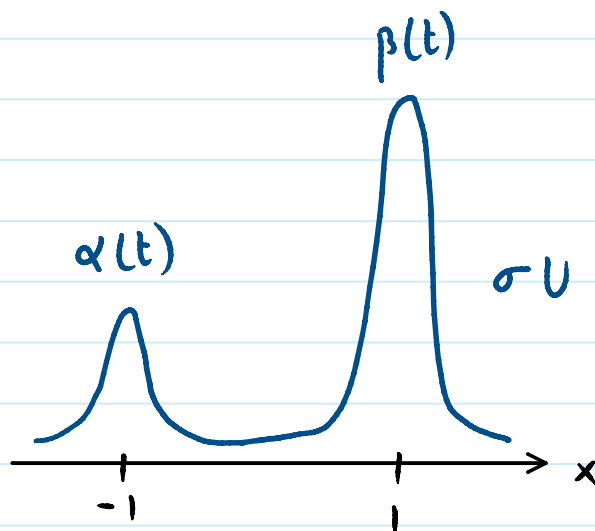
Here δ_x is the dirac delta at x
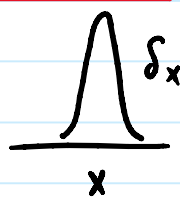
What this means is that, as our zooming factor ε goes to 0, our solution of (K-S) (multiplied by σ) converges to two spikes, of height $\alpha(t)$ and $\beta(t)$

Picture:

t fixed

If you think about it, it sort of makes sense, because remember that $\sigma = C\, e^{-H(x)/\varepsilon}$, so for every x except for -1 and

1, $H(x) > 0$, so for every x except -1 and 1, $\sigma \to 0$, which means sigma concentrates at $x = +/- 1$

(Proof of this actually uses energy methods: You multiply (K-S) by u to get one identity, and then by u_t to get another one, and you use some results from analysis)

This is already cool because it explains how to go from 2 variables to 1 variable, but what's more interesting is to find the PDE that α and β solve:

2) α and β solve (R-D) with $k = \dfrac{\sqrt{-H''(0)H''(1)}}{2\pi}$

A-MA-ZING, because not only does that tell us that the two PDE are related, but it also gives us a way of calculating k in terms of our potential H
(Recall our problem from the beginning: It's a big deal in chemistry to figure out what k is. So once you know H, it becomes easy to do so!)

III- IDEA OF PROOF

Let me give you an idea of the proof of 2), because it's a great illustration of the energy method! (just to show you that the methods learned in class ARE useful!)

Start with (K-S):

$$\sigma\, u_t = \left(\frac{\sigma}{\tau}\, u_x \right)_x$$

It turns out that the σ/τ term is BAD because it blows up near -1 and 1. So what do you do with a term you don't like?

You KILL it! (muahahahaha)

Let $\boxed{\phi(x) = \int_0^x \dfrac{\tau}{\sigma(y)}\, dy}$ (antiderivative of τ/σ)

Multiply your PDE by phi and integrate over, say $(-3/2, 3/2)$ (because all your terms are ok at $-3/2$ and $3/2$)

So we get:

$$\underbrace{\int_{-3/2}^{3/2} \sigma\, u_t\, \phi\, dx}_{\text{\textcircled{A}}} = \underbrace{\int_{-3/2}^{3/2} \left(\frac{\sigma}{\tau}\, u_x\right)_x \phi\, dx}_{\text{\textcircled{B}}}$$

STUDY OF A

Remember that

$$\sigma u \;\rightarrow\; a\delta_{-1} + \beta\delta_1$$

And in fact we also have

$$\sigma u_t \;\rightarrow\; a_t\delta_{-1} + \beta_t\delta_1$$

This says that σu_t concentrates at -1 and 1 with spikes $a(t)$ and $\beta(t)$

So in fact

$$A = \int_{-3/2}^{3/2} \sigma\, u_t\, \phi\, dx$$

$-3/2$

$\rightarrow \quad \alpha_t\, \phi(-1) + \beta_t\, \phi(1)$

But $\phi(1) = \displaystyle\int_0^1 \frac{\tau}{\sigma} = 1/k$

(can show this using "Laplace's method")

And by symmetry $\phi(-1) = \displaystyle\int_0^{-1} \frac{\tau}{\sigma} = -1/k$

So get $A \rightarrow \alpha_t\, (-1/k) + \beta_t\, (1/k)$

$$= (1/k)\, (-\alpha_t + \beta_t)$$

STUDY OF B

$B = \displaystyle\int_{-3/2}^{3/2} \left(\frac{\sigma}{\tau}\, u_x \right)_x \phi \; dx$

$= $ IBP

$= \; - \displaystyle\int_{-3/2}^{3/2} \frac{\sigma}{\tau}\, u_x \; \phi_x \; dx$

But remember $\phi(x) = \displaystyle\int_0^x \frac{\tau}{\sigma}$

$= \; - \displaystyle\int_{-3/2}^{3/2} \frac{\sigma}{\tau}\, u_x \, \frac{\tau}{\sigma}$

$$= - \int_{-3/2}^{3/2} u_x(x,t)\, dx$$

$$= u(-3/2, t) - u(3/2, t)$$

(NO MORE BAD TERMS, WOOOHOO!!!)

$\rightarrow 2\alpha - 2\beta$ (can show this using our estimates)

And so, in the limit, A = B

$\Rightarrow \quad 1/k \,(-\alpha_t + \beta_t) = 2\alpha - 2\beta$

$\Rightarrow \quad \alpha_t - \beta_t = 2k \,(\beta - \alpha)$

On the other hand, you can simply integrate (K-S) and get

$$\alpha_t + \beta_t = 0$$
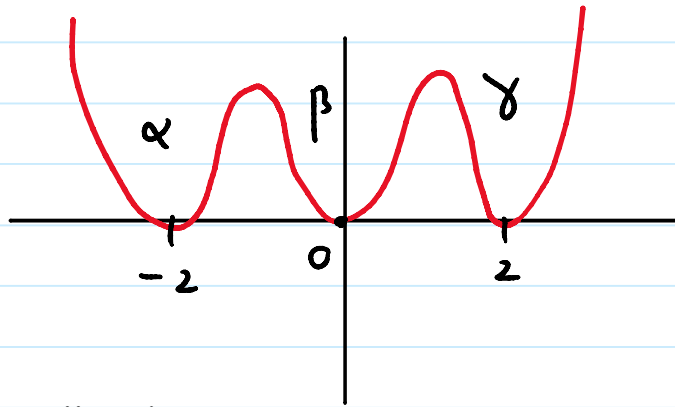
And so, adding/subtracting the equations gives

$$\begin{cases} \alpha_t = k(\beta - \alpha) & \text{(R-D)} \\ \beta_t = k(\alpha - \beta) \end{cases}$$

IV- VARIATIONS

What's nice about this proof is that it's flexible enough to adapt it to more complicated situations. Let me give you a couple of interesting variations
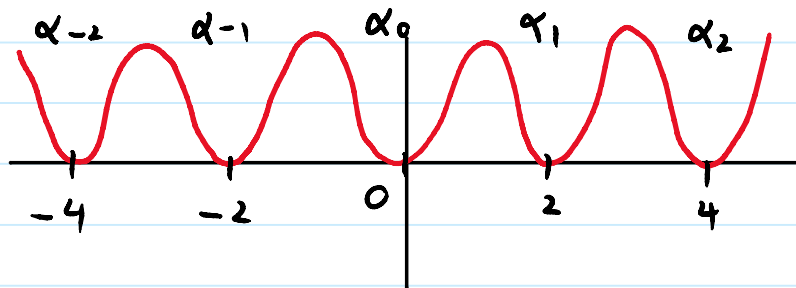
If H has 3 wells, then we get

$\sigma u \to \alpha \delta_{-2} + \beta \delta_0 + \gamma \delta_2$, where

$$\begin{cases} \alpha_t = k(\beta - \alpha) \\ \beta_t = k(\alpha - 2\beta + \gamma) \\ \gamma_t = k(\beta - \gamma) \end{cases}$$

In other words, each well interacts with its nearest neighbor. But for beta, since there are 2 interactions ($\alpha \leftrightarrow \beta$ and $\beta \leftrightarrow \delta$), we have this extra factor of 2

B) INFINITELY MANY WELLS

Get $\sigma u \to \sum_{m} \alpha_m \delta_{2m}$ where

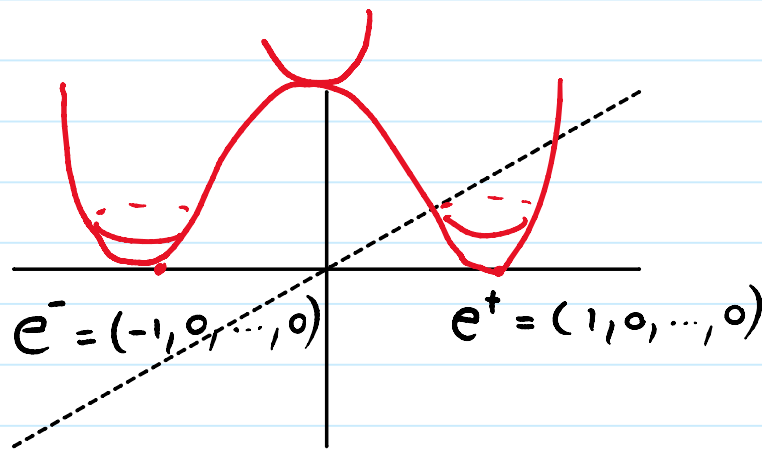$(\alpha_m)_t = k(\alpha_{m-1} - 2\alpha_m + \alpha_{m+1})$

(Again, interaction between the nearest neighbors)

The true miracle is that we can generalize this to the case where x is more than 1 dimensional

Suppose H has wells at $(-1,0,0,...,0)$ and $(1,0,0,...,0)$ and a saddle at 0

Picture

$e^- = (-1,0,...,0)$ $e^+ = (1,0,...,0)$

Then (K-S) becomes

$$\sigma\, u_t = \operatorname{div}\left(\frac{\sigma}{\tau}\,\nabla u\right)$$

And we get the same result:

$$\sigma u \quad \rightarrow \quad \alpha\, \delta_{e-} + \beta\, \delta_{e+}$$

Where α and β solve

$$\begin{cases} \alpha_t = k(\beta-\alpha) \\ \beta_t = k(\alpha-\beta) \end{cases}$$

SAME equation, but here k is more complicated

What's interesting is that this time, instead of defining ϕ explicitly, we define it with a PDE. So you're literally using a PDE to solve a PDE (YO DAWG!!!)

Finally, people always ask me: Peyam, is this useful at all? Of course it is!

It's useful,
At least for me,
Because it's the PDE,
That got me the PhD!!!

And this officially concludes our PDE adventure! I would like to thank you for flying Peyam Airlines, it's been a true pleasure having you on board, and I wish you a safe onward journey!