

## LECTURE 10: CHEMICAL REACTIONS AND DIFFUSIONS

**Reading:** The notes below

**Video:** The PDE that gave me the PhD

Welcome to the last lecture of our PDE adventure! Today, to end on a sweet note, we'll talk about the PDE I studied for my thesis, or, as I like to call it, the PDE that gave me the PhD. More precisely, explore an equation (or a set of equations) that model chemical reactions. And don't worry, you don't need to know any chemistry to do this, the only prereq for this is Breaking Bad ☺

### 1. THE GREAT DEBATE

Consider a simple chemical reaction  $A \rightleftharpoons B$ , 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 careful note: We are **NOT** studying  $C + O_2 = CO_2$ , this is already too complicated; we're just studying one molecule transforming into another)

Then there are two ways of viewing this reaction:

**1.1. Macroscopic Level.** On the one hand, on the macroscopic level, you can simply say that there are only two molecules A and B, and you can look at their respective concentrations  $\alpha$  and  $\beta$

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*Date:* Monday, June 1, 2020.

$\alpha = \alpha(t)$  = concentration of A at time t

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

Then  $\alpha$  and  $\beta$  satisfy the following differential equation, called the **reaction-diffusion system**:

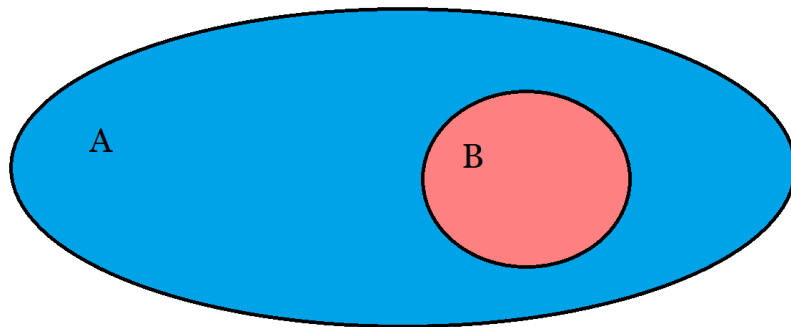
**Reaction-Diffusion System:**

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

Here  $\alpha_t$  and  $\beta_t$  are the time derivatives of  $\alpha$  and  $\beta$ , and  $k > 0$  (or kappa) is a positive constant, called the reaction-rate constant.

**Note:** It's a **BIG** deal in chemistry to figure out what  $k$  is.

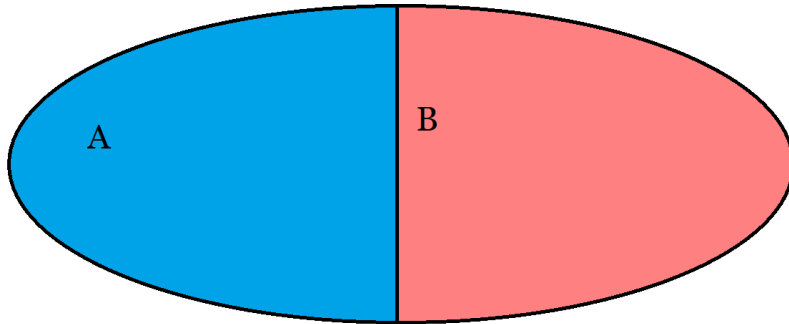
Intuitively (R-D) says the following: If there are more  $A$  molecules than  $B$  molecules, like in the following sample:



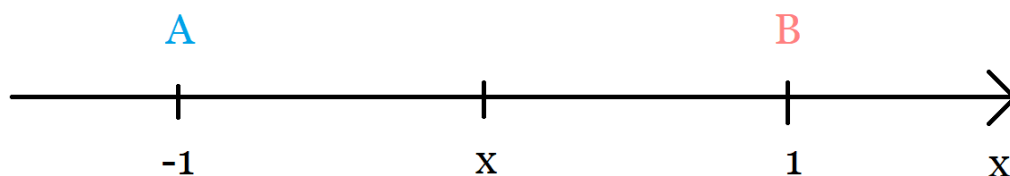
Then  $\alpha > \beta$ ,  $\beta - \alpha < 0$ , so  $\alpha_t = k(\beta - \alpha) < 0$ , so  $\alpha$  decreases, so  $A$  decreases

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

And therefore (R-D) says that there is a constant interplay between  $A$  and  $B$ , until at some point you reach equilibrium:



**1.2. Microscopic Level.** On the other hand, on the microscopic level, instead of just having two states  $A$  and  $B$ , you can actually think of the molecule as having a continuum of states, like a string:



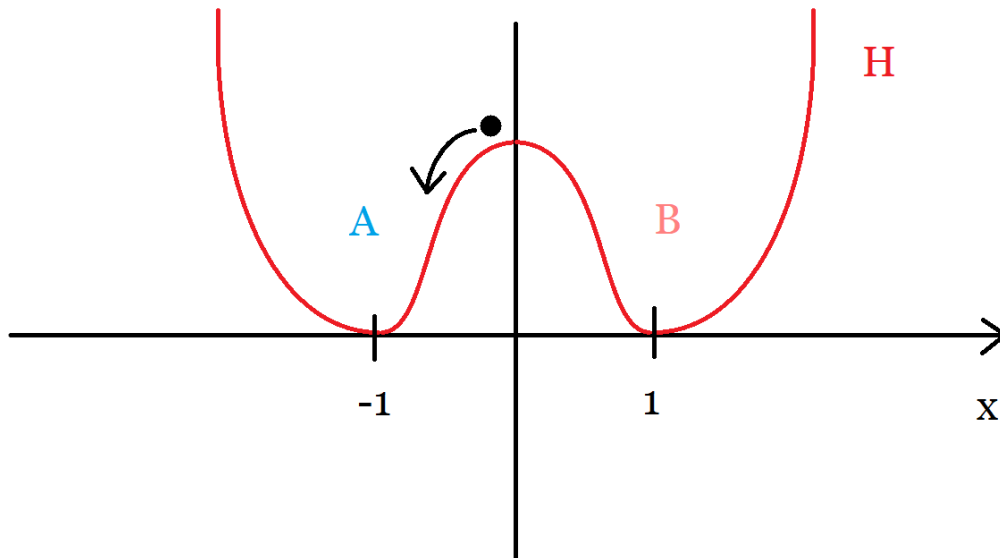
Where on the left endpoint you have  $A$  and on the right endpoint you have  $B$ , with infinitely many hybrid states in between

We can parametrize those states with a new *chemical* variable  $x$ , where  $x = -1$  corresponds to  $A$  and  $x = 1$  corresponds to  $B$  (and  $x = 0$  for example would be a weird hybrid between  $A$  and  $B$ ). Think of  $x$  as a chemical position.

Again, with the protein analogy, think of  $x$  as the angle of the twist.

What's nice about this interpretation is that now we can give a probabilistic flavor of chemical reactions.

Namely, you can now think of the molecule as a marble that swings back and forth on (what's called) a double-well potential function  $H$ :



Here the two wells of  $H$  correspond to  $A$  and  $B$ , and a chemical reaction is just the passage from  $A$  to  $B$ .

(Assumptions: Even, local max at 0, local min at  $\pm 1$ )

On the potential, the marble performs Brownian Motion (= drunken motion), and in particular we can model its behavior using a PDE called the **Kramers-Smoluchowski equation**:

**Disclaimer:** What I'm about to write down won't make any sense to you, but I'll spend the next 10 minutes explaining the terms)

**Kramers-Smoluchowski Equation:**

(K-S)  $\sigma u_t = (\sigma u_x)_x$

Here:

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

Tells you roughly how many particles there are at  $x$  and  $t$ , and  $u_x$  is the derivative with respect to  $x$

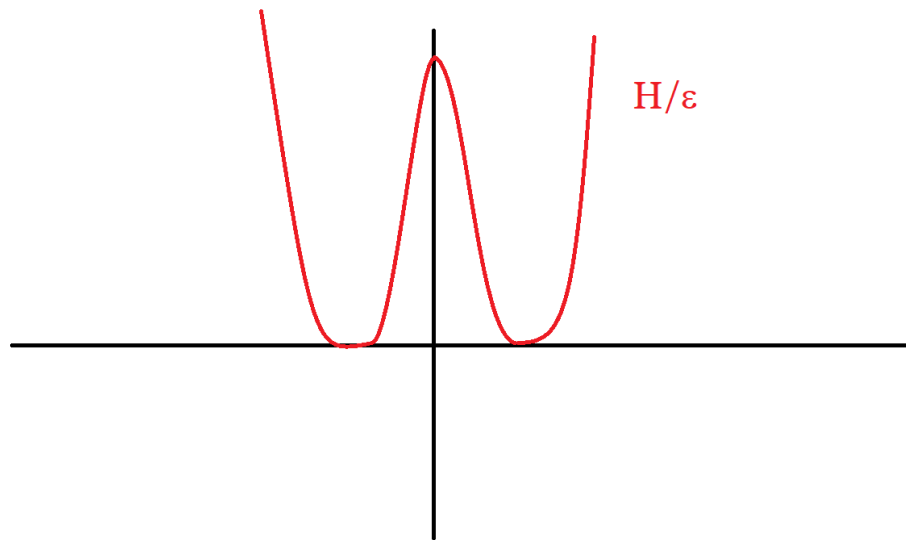
Moreover, although I have not explicitly written it here, everything depends on  $\epsilon$ , where:

(2)  $\epsilon =$  Zooming factor

$\epsilon = 0$  is the macroscopic state,  $\epsilon > 0$  is the microscopic state

(3)  $\sigma = \sigma(x) = e^{-\frac{H(x)}{\epsilon}}$

Think of it as  $H$ , but we scale it by  $\epsilon$  to make it **HARD** to go from  $A$  to  $B$ , and we exponentiated it to make it nicer.



(Also, technically you have to multiply this by a constant so that the total mass of  $\sigma$  is 1)

(And strictly speaking, you have to divide the right-hand-side by a constant  $\tau$  that makes this work)

I know this looks like complete gibberish, but if you ignore  $\sigma$  in the equation, then you get  $u_t = u_{xx}$ , which is a classical PDE called the heat equation! So all that it is 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 claim that 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 two different sides of the same

coin!

## 2. MAIN RESULT

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

**SAY WHAT???** How are the two equations *possibly* related? In (K-S), you have *one* function  $u$  that depends on  $x$  and  $t$ , whereas in (R-D) you have *two* functions  $\alpha$  and  $\beta$  that only depend on  $t$ .

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

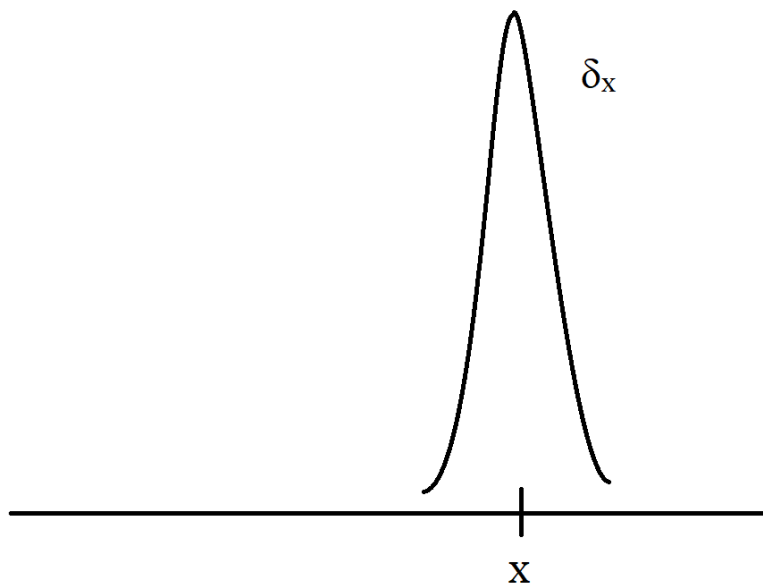
### Main Theorem (Part 1):

As  $\epsilon$  goes to 0, we have:

$$\sigma(x)u(x, t) \rightarrow \alpha(t)\delta_{-1} + \beta(t)\delta_1$$

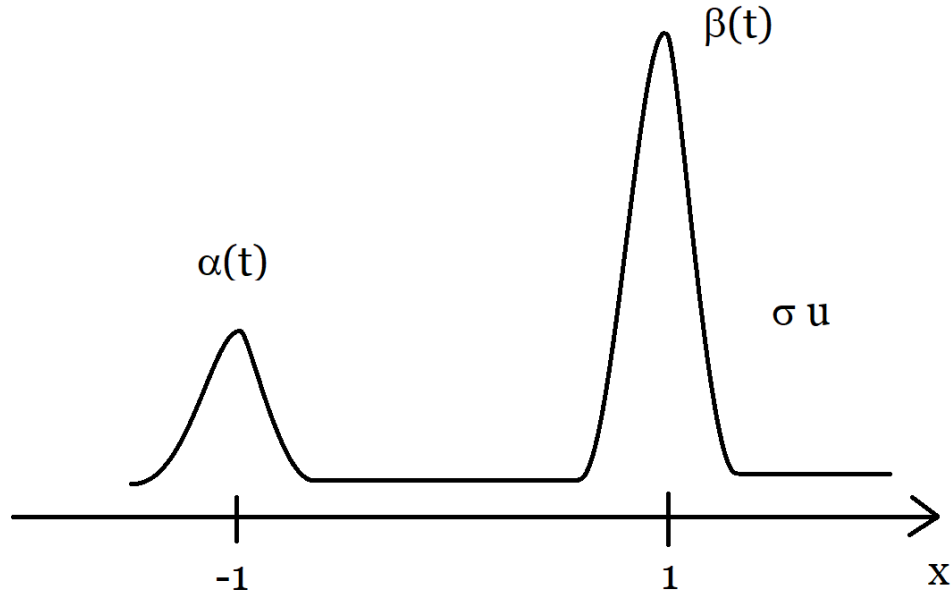
**Note:** Here  $\delta_{-1}$  is the dirac delta at  $x = -1$ , infinite spike at  $-1$ :





What is this saying? It is saying that, as our zooming factor  $\epsilon$  goes to 0, our solution of (K-S) (multiplied by  $\sigma$ ) 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 for  $x \neq \pm 1$ ,  $H(x) > 0$ , and therefore  $\sigma = e^{-\frac{H(x)}{\epsilon}} \rightarrow 0$  except for  $\pm 1$ , so  $\sigma$  concentrates at  $x = \pm 1$ .

In case you're curious, the proof of this uses a standard PDE method called the energy method: You multiply (K-S) by  $u$  and integrate by parts to get one identity, and then by  $u_t$  to get another identity, and then you use some compactness results in functional analysis.

This result is already neat because it explains how we go from 2 variables  $x$  and  $t$  to one variable  $t$ , but what's more interesting is to find the PDE that  $\alpha$  and  $\beta$  solve. Because remember that the main goal is to show how (K-S) and (R-D) are connected.

**Main Theorem (Part 2):**

$\alpha$  and  $\beta$  (the limit functions) solve (R-D) with

$$k = \frac{\sqrt{-H''(0)H''(1)}}{2\pi}$$

**A-MA-ZING**, because it not only tells us that the *PDE* are related, but it also gives us a way of calculating  $k$  in terms of our potential  $H$  !

Because remember one of the problems I posed at 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! And in fact there are some numerical methods that approximately calculate what  $H$  is.

### 3. IDEA OF PROOF

Let me give you an idea of the proof of (2) because it's not only really neat, but also (as they say) even a calculus student can do this, because it requires a simple integration by parts.

**Note:** There are other, more complicated proofs of this, some of which use  $\Gamma$  convergence, which Giovanni Leoni at CMU is an expert of, and others use Wasserstein spaces, but what makes this proof nice is its simplicity.

Start with (K-S):

$$\sigma u_t = (\sigma u_x)_x$$

It turns out that the  $\sigma$  term is **BAD** because it blows up near  $\pm 1$ . So what do you do in math with a term that you don't like? You **KILL**

it! (muahahaha >:) )

Here we would like a function whose derivative is  $\frac{1}{\sigma}$ , so naturally:

Let  $\phi(x) = \int_0^x \frac{1}{\sigma(y)} dy$  (antiderivative of  $\frac{1}{\sigma}$ )

Multiply your PDE by  $\phi$  and integrate over, say  $(-\frac{3}{2}, \frac{3}{2})$  (because all your terms are ok near  $\pm\frac{3}{2}$ )

Hence we get:

$$\int_{-\frac{3}{2}}^{\frac{3}{2}} \sigma u_t \phi dx = \int_{-\frac{3}{2}}^{\frac{3}{2}} (\sigma u_x)_x \phi dx$$

$$A = B$$

**3.1. Study of A.** Remember that

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

Now let me do something that will give analysts a heart-attack: Let's differentiate this identity with respect to  $t$ :

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

(NOT OBVIOUS, but can show this with separate methods)

This says that  $\sigma u_t$  concentrates at  $\pm 1$  with spikes  $\alpha(t)$  and  $\beta(t)$ .

So in fact:

$$A = \int_{-\frac{3}{2}}^{\frac{3}{2}} \sigma u_t \phi dx \rightarrow \alpha_t \phi(-1) + \beta_t \phi(1)$$

But

$$\phi(1) = \int_0^1 \frac{1}{\sigma} \rightarrow \frac{1}{k}$$

Can show this using a Taylor expansion near 0 and a Laplace expansion near 1, which explains how  $H''(0)$  and  $H''(1)$  contribute to this (You also need the two constants that I swept under the rug)

And by symmetry

$$\phi(-1) = \int_0^{-1} \frac{1}{\sigma} dx \rightarrow -\frac{1}{k}$$

Therefore:

$$A \rightarrow \alpha_t \left( -\frac{1}{k} \right) + \beta_t \left( \frac{1}{k} \right) = \frac{1}{k} (-\alpha_t + \beta_t)$$

### 3.2. Study of $B$ .

$$B = \int_{-\frac{3}{2}}^{\frac{3}{2}} (\sigma u_x)_x \phi dx$$

IBP (assume no terms at endpoints, technically use a cutoff function)

$$= - \int_{-\frac{3}{2}}^{\frac{3}{2}} \sigma u_x \phi_x dx$$

Remember  $\phi(x)$  is an antiderivative of  $\frac{1}{\sigma}$

$$= - \int_{-\frac{3}{2}}^{\frac{3}{2}} \sigma u_x \frac{1}{\sigma} dx$$

$$= - \int_{-\frac{3}{2}}^{\frac{3}{2}} u_x dx$$

(The war is over)

$$= u \left( -\frac{3}{2}, t \right) - u \left( \frac{3}{2}, t \right)$$

$$\rightarrow 2\alpha - 2\beta$$

(Can show using out estimates)

### 3.3. Combining the two. And so, in the limit:

$$A = B$$

$$\Rightarrow \frac{1}{k} (-\alpha_t + \beta_t) = 2\alpha - 2\beta$$

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

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

$$\alpha_t + \beta_t = 0$$

And so, adding/subtracting the equations, we get:

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

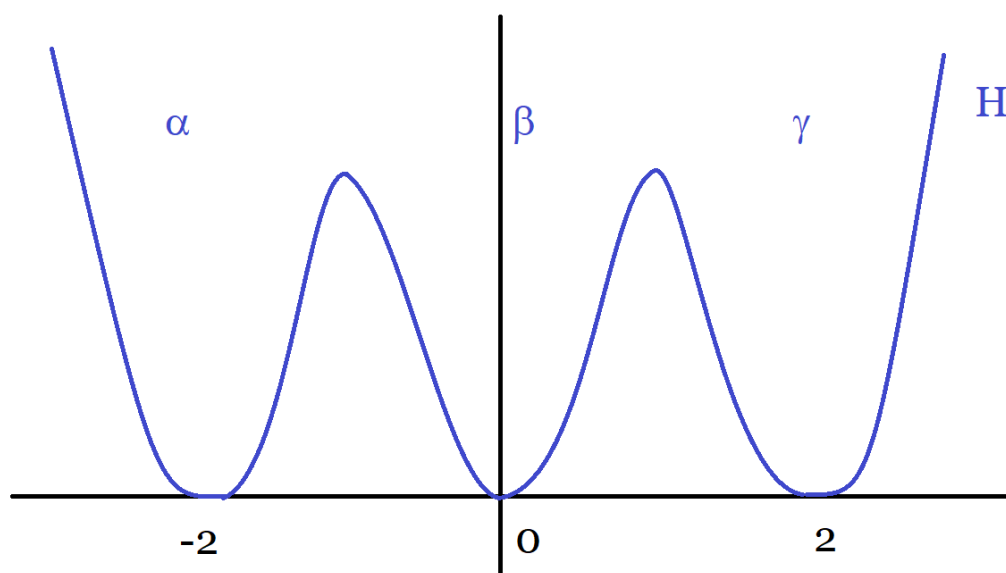
Which is (R-D) !!!

□

#### 4. VARIATIONS

What's nice about this proof is that it's flexible enough to adapt it to more complicated situations. Let me give you some interesting variations:

##### 4.1. Triple Wells.



If  $H$  has 3 wells, then we get:

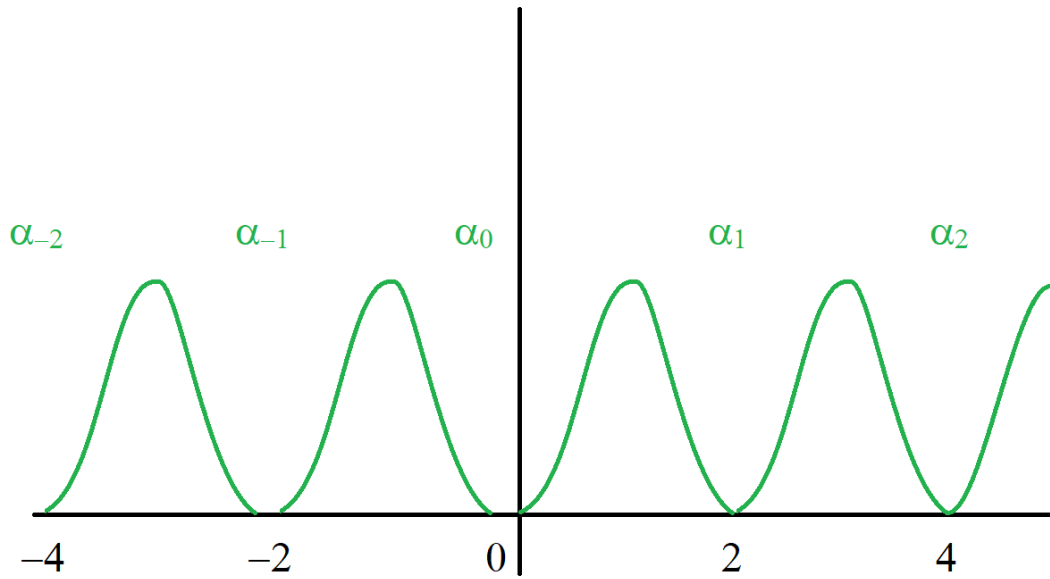
$$\sigma u \rightarrow \alpha \delta_{-2} + \beta \delta_0 + \gamma \delta_2$$

Where:

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

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

#### 4.2. Infinitely many wells.



If  $H$  has infinitely many wells, then we get:

$$\sigma u \rightarrow \sum_m \alpha_m \delta_{2m}$$

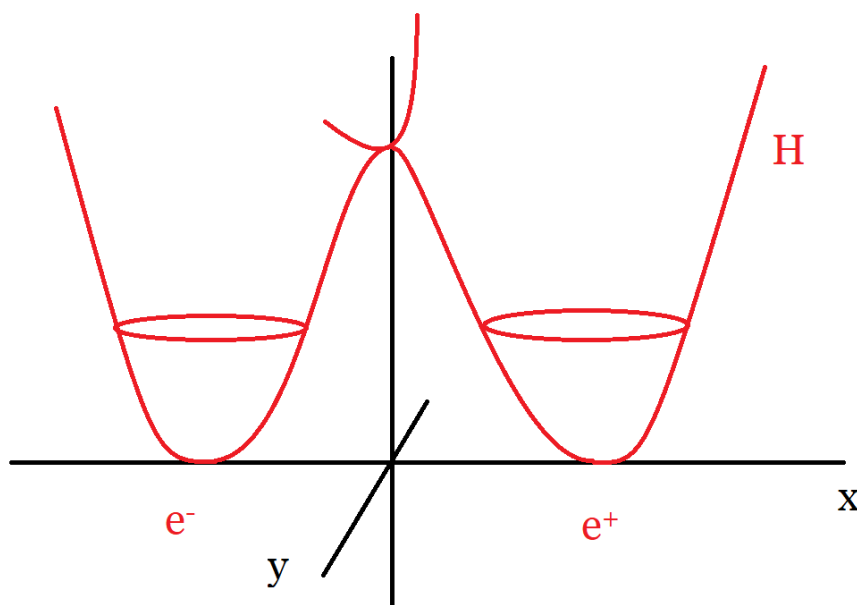
Where:

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



**4.3. Higher Dimensions.** The true miracle is that we can generalize this to the case where  $x$  is more than 1-dimensional!

Suppose  $H$  has wells at  $e^- = (-1, 0, \dots, 0)$  and  $e^+ = (1, 0, \dots, 0)$  and a saddle at  $O$



Then (K-S) becomes:

$$\sigma u_t = \operatorname{div}(\sigma \nabla u)$$

And we get the same result:

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

Where  $\alpha$  and  $\beta$  solve

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

**SAME** equation, but this time  $k$  is more complicated (depends on the eigenvalues of  $D^2H$  at  $O$ )

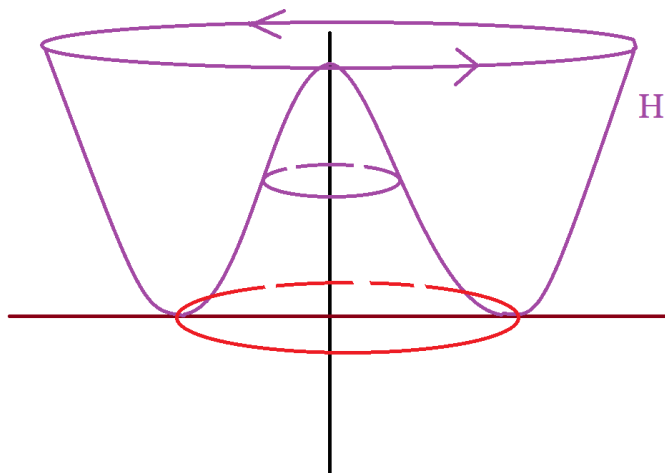
What's interesting is that this time, instead of defining  $\phi$  explicitly, we define it with a PDE. So you're literally using a PDE to solve a PDE!

**4.4. Current and Open Projects.** Now of course, one natural extension is: What if we're in the higher dimensional case, but this time we have three potentials? If they are symmetric, then it's not a problem at all, you can just adapt the methods above.

But what if the potential is not symmetric at all? That is, the wells are just at 3 (or more) random locations? Then, even though the second part of the proof still works, we need to do much more work to prove the estimates and convergence from the first part. Luckily, in joint work with Insuk Seo from Seoul National University, we were able to solve this by using some probability theory, namely by interpreting the wells as states of a Markov process, and by using some results about (what are called) metastable random processes. So in some sense, the case of several wells in higher dimensions has been completely solved.

But what is really nice about this problem that we can generate a plethora of more open problems just by changing the potential function  $H$ . For instance, let me give you two interesting cases:

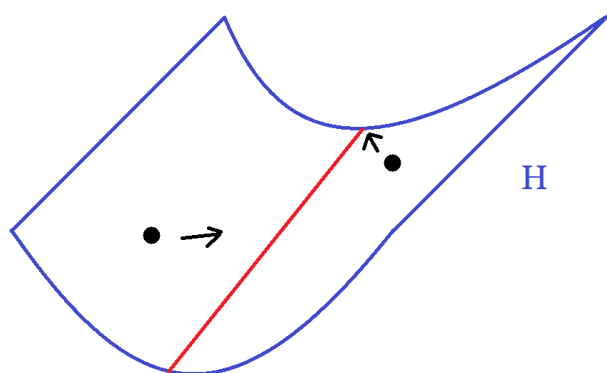
**Sombrero Problem:** What if you take  $H$ , but spin it around the  $z$ -axis to look like a sombrero?



Then there is a circle of wells, and you can show that  $\sigma u$  concentrates on that circle, but the interesting question is: What is the resulting PDE?

### Beaver Dam:

What if  $H$  looks like a (version) of a beaver dam, like that:



Then, sure,  $\sigma u$  concentrates on a line, but again it's interesting to see what the resulting PDE is, because the particle can not only go left and right, but also forward and backward (it is not trapped any more).

So you can see, for each  $H$ , you have your own little problem, and maybe you can come up with your favorite version of  $H$  as well!

Alright, with this I would like to thank you for flying Peyam airlines, I hope you had a pleasant stay on board, and I wish you a safe onward journey ☺