Running steady-state simulations with ACDC:

What do you need to consider when preparing the input files based on your data?

Quick guide by Tinja Olenius 20.5.2016

You have prepared two input files: the free energy file (.txt), and the system file (.inp), and you have codes for running basic ACDC simulations → **What next?**

1 You have to make sure that **your simulation system is reasonable**: it must be large enough, and the largest included clusters must have relatively low evaporation rates at the studied temperature.

2 You have to **set the boundary conditions** so that they are reasonable with respect to how the cluster growth proceeds inside your system.

There are no exact answers for how "reasonable" a system is –we have to assess it based on the existing data and our best understanding. This quick guide shows how to set up your simulation system so that you can trust that your results are reliable.

First, run the Perl script to generate the output (Matlab) files, and **examine the rate constants**. Here's an example of evaporation rates in the H_2SO_4–NH_3 system:

Overall evaporation at T = 280 K
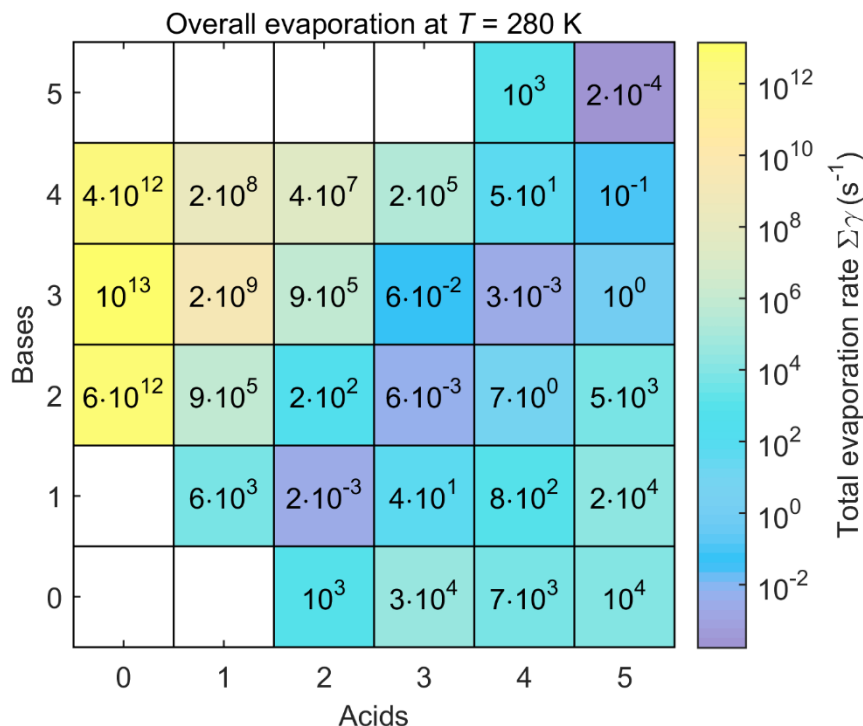
The idea is to see if the most stable clusters, especially **the largest clusters**, are stable enough (**= their evaporation rates are low**), so that we can safely assume that also the clusters outside the simulation system don't evaporate significantly, and we can let them grow out.

Looks okay, *e.g.* ~10^{-4} s^{-1} is a relatively low evaporation rate in atmospheric conditions
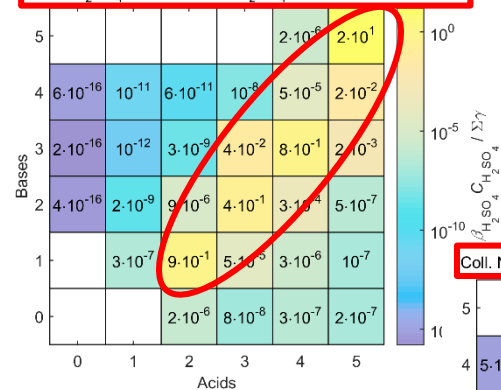
We still have to see that the evaporation frequencies of the outgrown clusters can be assumed to be low enough with respect to the vapor collision frequencies at the lowest studied vapor concentrations (at least ~1–2 orders of magnitude lower)

Looks good, too: the collisions seem to start dominating
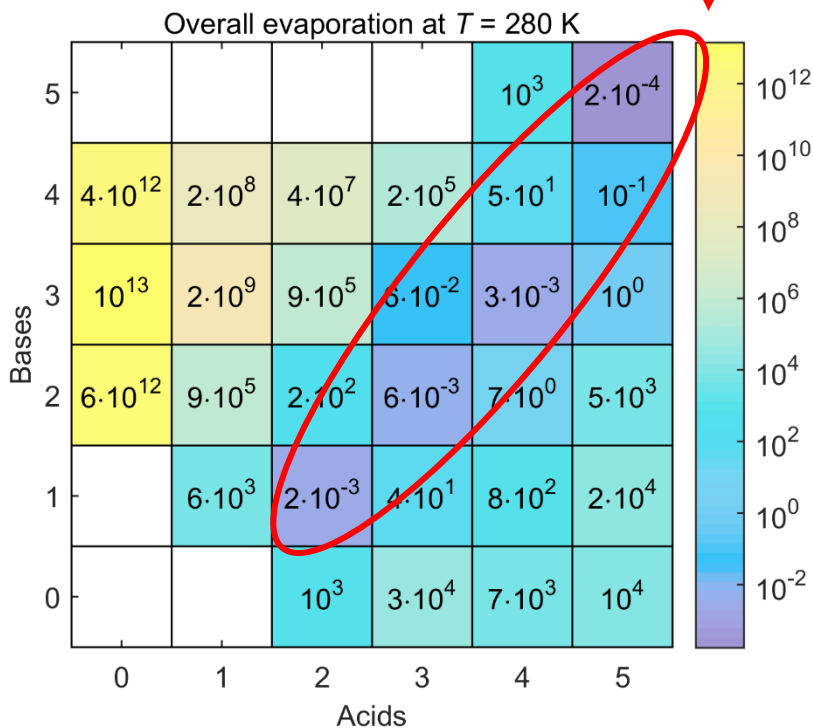
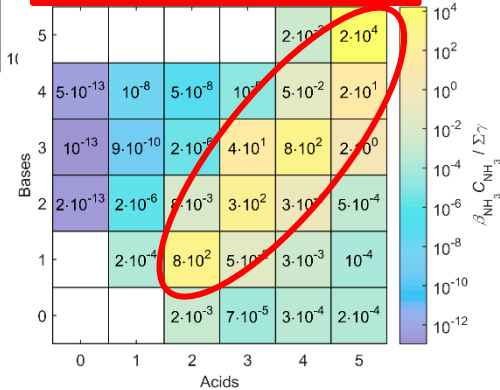Growth by H_2SO_4

Growth by NH_3

For those who like to think about the Gibbs free energies, you can also see*****
how **the actual ΔG surface** looks like at the given vapor concentrations:

Looks ok: ΔG seems to be decreasing

Actual ΔG at $[H_2SO_4] = 5 \cdot 10^6$ cm^{-3}, $[NH_3] = 100$ ppt, $T = 280$ K
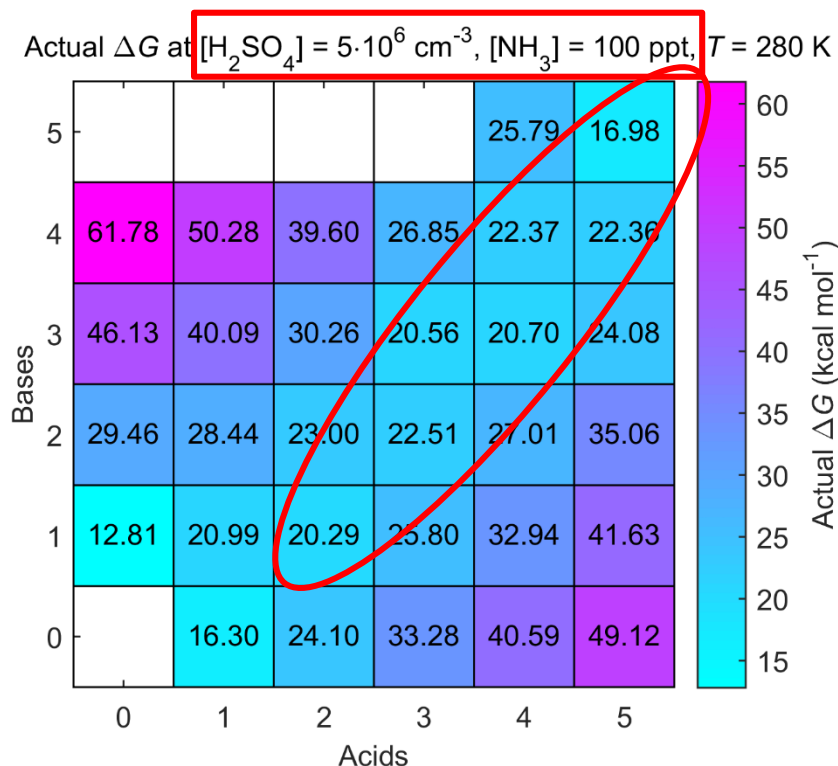
*But you don't need to look at this; it's
more robust to examine the rate constants

! NB: Don't mix these with **the reference ΔG_{ref}**
(= the values that you get from *e.g.* quantum
chemistry, and write into the ACDC input file);
they **don't help** you with this!

Standard ΔG_{ref} at $T = 280$ K

5
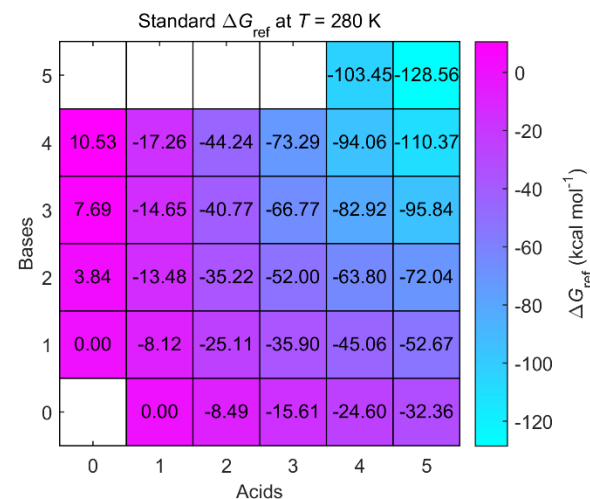
Now, you need to run the actual ACDC simulation with Matlab, and **examine the growth pathways**. For the H_2SO_4–NH_3 system, the pathways look like this in typical conditions:

$[H_2SO_4] = 5 \cdot 10^6$ cm^{-3}, $[NH_3] = 100$ ppt, $T = 280$ K, coag. sink
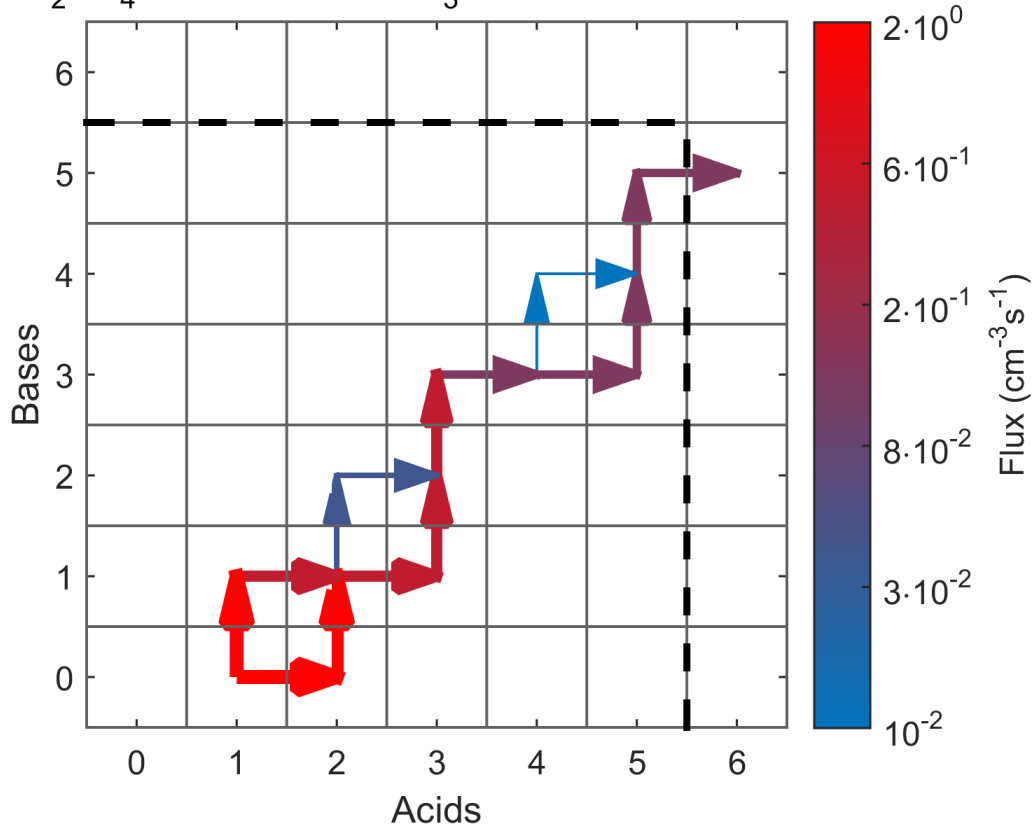

By seeing how the clusters inside your system grow, you can decide what are **the most likely growth routes** over the system boundary.

Of course you need to set a first guess for the boundary conditions in the .inp file; for binary systems with up to n and m molecules of components A and B, this can be *e.g.* n+1 A, m B

The main growth flux proceeds via **clusters that on the average have more acid than ammonia molecules**

$[H_2SO_4] = 5 \cdot 10^6$ cm^{-3}, $[NH_3] = 100$ ppt, $T = 280$ K, coag. sink
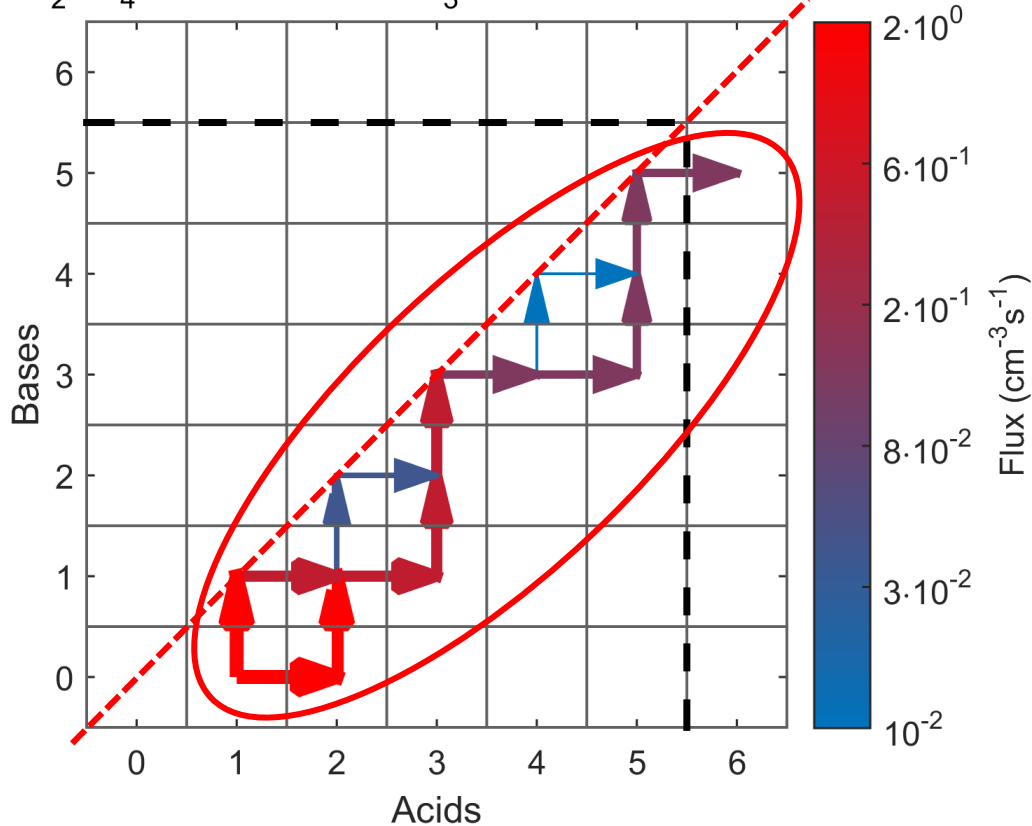
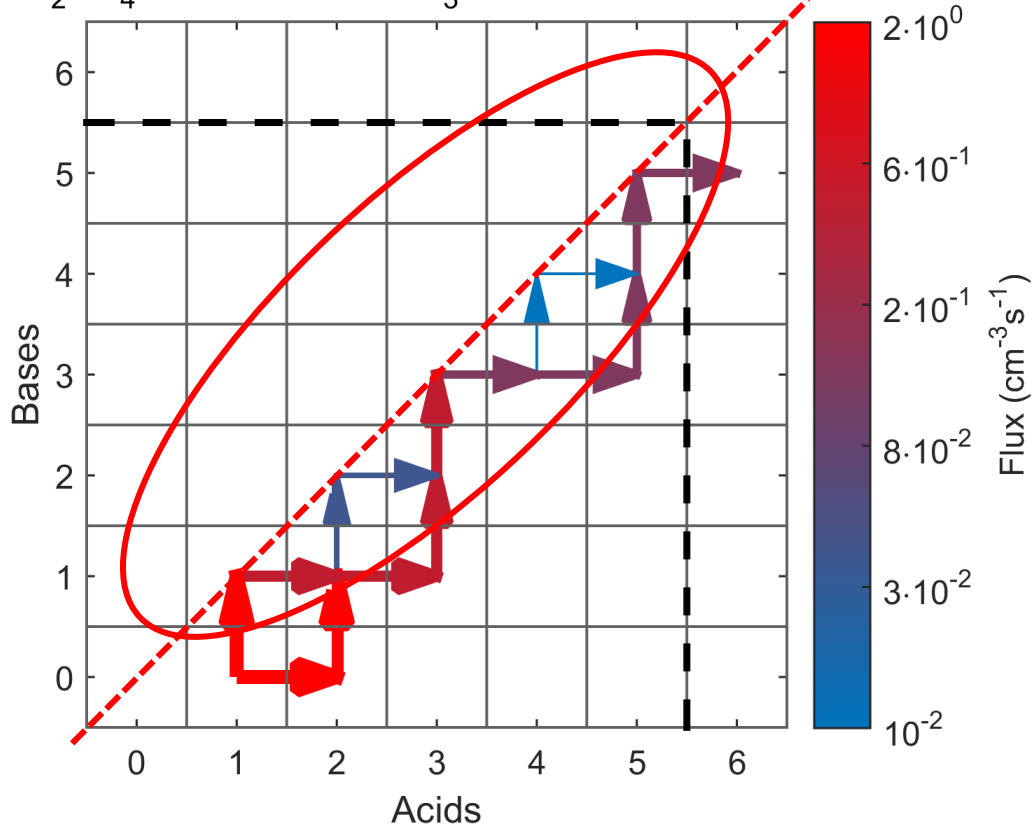→ 6 H$_2$SO$_4$ and 5 NH$_3$ **can** be considered a reasonable boundary condition

Note that you can set **more than one criteria** for the boundary conditions:
you can also let *e.g.* clusters that have at least 5 acids and 6 ammonias grow out of the system

$[H_2SO_4] = 5 \cdot 10^6$ cm^{-3}, $[NH_3] = 100$ ppt, $T = 280$ K, coag. sink

→ But 5 H_2SO_4 and 6 NH_3 **cannot** be considered a reasonable boundary condition, because clusters containing more NH_3 than H_2SO_4 are relatively unstable, and are not involved in the growth inside the system

Your system is set now!

1 Clusters that are let to grow out are much more likely to keep growing than to evaporate back towards smaller sizes

2 Based on the trends inside the system, we decided what are the best boundary conditions, and excluded the boundary condition candidates that did not seem plausible

You can be confident that the simulation results will be reliable, and not just some nonsense or distorted by a bad choice of boundary conditions.