# Chamber model: validation

## Condensation

It is known that for a narrow particle distribution, the count median diameter (CMD) of particles grows about by condensation of sulphuric acid alone when the vapour concentration has a constant value of and the saturation vapour pressure is assumed negligible. (lähde?). This growth velocity serves as a reference for the chamber model validation tests.

To simulate the condensation growth, the chamber model was initialized so that neither coagulation nor dilution happens. The initial vapour concentration was set to constant so that the value does not change despite the condensation. The size distribution consists of 100 sections between diameters and . The geometric standard deviation (sigma) was 1.01, making the distribution nearly monodispersive, and the mean diameter was varied between 2 nm and 20 nm. The time vector begins from zero seconds and goes to 7200 seconds with steps of 10 seconds. Hence, the model predicts how much the count median diameter grows in two hours.

At first, the predictions were too low: the growth velocities for different diameters were about . The reason was the density of particulate matter which was set to . This is the density of sulphuric acid and should give the right predictions. However, the sulphuric acid molecules do not condensate alone on the surface of particles but there is also water molecules bound to sulphuric acid molecules. Thus the density of condensing molecules is nearer to the density of water than that of sulphuric acid.

After changing the particle matter density from to (density of water) the model gave predictions that matched the reference growth velocity: the average change of the count median diameter for different monodispersive distributions was about . The parameters that differ from default parameters are listed in table 1 and results in table 2.

Table : Simulation parameters

|  |  |
| --- | --- |
| Parameter | Value |
| Cvap0 | 1.38E10 1/cm^3 |
| Cvap\_const | 1 |
| coag\_on | 0 |
| dilu\_on | 0 |
| tvect | 0:10:7200 |
| Dp\_min | -10 |
| Dp\_max | -6 |
| sigma | 1.01 |
| sections | 200 |
| output\_sections | 2000 |
| Cvap\_tol | 10 1/cm^3 |
| Dp\_tol | 0.01E-9 m |
| particle\_dens | 1.0 g/cm^3 |

Table : Simulation results

|  |  |  |
| --- | --- | --- |
| µ of distribution (nm) | Growth velocity of CMD (nm/h) | Error |
| 2 | 1.05 | 5 % |
| 11 | 1.07 | 7 % |
| 20 | 1.01 | 1 % |
| Average | 1.04 | 4 % |

The average error of growth velocity given by the model compared to the reference value of was 4 % when the initial particle diameter ranged from 2 nm to 20 nm. The model growth velocity was always higher than the reference velocity.

## Coagulation

For a monodisperse particle distribution, the change of particle concentration caused by coagulation is

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | , | (1) |
|  |  |  |  |

when the coagulation coefficient,, is constant (Seinfeld & Pandis 2006). Thus, if ,

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | , | (2) |
|  |  |  |  |

and has decreased to half of the initial value in time

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | . | (3) |
|  |  |  |  |

We can simulate the case of monodisperse aerosol coagulation by creating a very narrow particle distribution. In the beginning the distribution is so narrow that the particles coagulate only with same-sized particles and the coagulation coefficient is constant. However, the distribution starts to widen and the average size of particles starts to increase as coagulation goes on. As a following, the coagulation coefficient does not stay constant under simulation and equation (1) does not perfectly predict the change of particle concentration.

In this simulation a narrow distribution was created to model a monodispersive aerosol. The simulation time was 5000 seconds and initial particle concentration . Under these conditions the coagulation did not significantly widen the distribution or change the count median diameter, so it can be assumed that the coagulation coefficient between particles was approximately constant and so it is justified to use equation (3) to calculate the reference half time.

The simulation was run for six different initial mean diameters of particles ranging from 2 nm to 20 µm. The reference half time of number concentration was calculated using equation (3). The coagulation coefficient in the equation was calculated in the same way as the chamber model calculates it and the diameter used in calculation was the mean diameter of the same distribution that was used in simulation. Also the initial number concentration used in equation (3) was the same as the initial number concentration of the distribution.

The used parameters that differ from default parameters are listed in table 3. Parameter “mu” had values from 2 nm to 200 µm.

Table

|  |  |
| --- | --- |
| Parameter | Value |
| dilu\_on | 0 |
| Cvap0 | 0 |
| gas\_source | 0 |
| N | 1E6 |
| sigma | 1.01 |
| sections | 1000 |
| output\_sections | 10000 |
| N\_tol | 0.01 |

The number concentration half times of simulated coagulation () and reference half times () are in table 4.

Table

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Initial mean diameter |  |  |  | error |
| 2 nm | 3053 | 2812 | 241 | 7.9 % |
| 20 nm | 1068 | 1016 | 52 | 4.9 % |
| 200 nm | 2015 | 2050 | -35 | 1.7 % |
| 2 µm | 3182 | 3160 | 22 | 0.7 % |
| 20 µm | 3352 | 3317 | 35 | 1.0 % |
| 200 µm | 3361 | 3326 | 35 | 1.0 % |

Simulated coagulation half times differ from reference half times by % in average. The difference is explained by the assumptions of equation (3) that the coagulation coefficient is constant and that the particle distribution is monodisperse. In all but one cases the half time of simulated coagulation is shorter than the reference half time. This is caused by the fact that even though the distribution is very narrow in the beginning of the simulation, the coagulation widens it fast and soon the aerosol is not monodisperse anymore. Because the coagulation of polydisperse aerosol is faster than that of monodisperse aerosol, the half time decreases.

The distribution with initial mean diameter of 200 nm is an exception: the half time of simulated coagulation is longer than the reference half time. The reason is coagulation coefficient. The reference half time was calculated with equation (3) and the coagulation coefficient was assumed to be a constant. However, when the particle diameter is around 200 nm, the coagulation coefficient decreases relatively fast when the diameter grows. In the simulation, the particle diameter grows by coagulation and therefore also the coagulation coefficient decreases, making the coagulation process slower. That is why the reference half time that was calculated with initial coagulation coefficient is shorter than the real half time.

## Mass conservation

If an aerosol does not dilute or deposit and there is no particle or gas sources, the total mass of particles and gas should not change even if coagulation reduces particle concentration and condensation grows particles. In condensation the mass of vapour decreases but the mass of particles increase as much. This was tested by running the simulation without vapour source and dilution and deposition turned off, and the model did conserve the total mass.

When dilution and deposition are turned on, some of the total mass disappears by dilution of gas, dilution of aerosol particles and deposition of particles. However, the model keeps track of the diluted and deposited molecules and therefore it is possible to calculate the diluted and deposited mass.

If a vapour source exists, the increase of mass in the system is , where M is the molar mass of vapour and is Avogadro’s number.

The mass of the system in the beginning is

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | . | (4) |
|  |  |  |  |

In the end, the total mass (including diluted and deposited mass) is

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | . | (5) |
|  |  |  |  |

On the other hand, as the vapour source is the only source of mass, the total mass in the end can be written also:

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | . | (6) |
|  |  |  |  |

The value can be exported from chamber model’s calculated data after simulation run and the value of can be calculated by hand using the initial parameters of simulation. When the model is working properly, the value got from simulation should equal the value calculated with equation (6).

The simulation was run for 10800 seconds with different initial parameters, and both and were calculated for 3 different cases. In all cases the number of sections was 300 and the number of output data sections 3000. The initial parameters are shown in table 5 and the results in table 6.

Table : Initial parameters.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Case | Initial vapour concentration | Vapour source | Sedimentation | Dilution |
| 1 | off | off | off | off |
| 2 | on | on | on | on |
| 3 | on | vector | on | vector |

Table : Results

|  |  |
| --- | --- |
| Case | error |
| 1 | 0.00 % |
| 2 | 0.04 % |
| 3 | 0.04 % |

The results in table 5 show that there is in practice no difference between the final mass of simulated aerosol and the calculated final mass, so the model conserves the total mass properly.