Documentation of ParScale's `modelEqn` Class

Contents

1 Nomenclature

1.1 Latin Characters

Variable	Unit	Meaning
a	$\mathrm{m^2\,s^{-1}}$	Thermal diffusivity
A	$\mathrm{m^2}$	Cross-sectional area
A, B, C, D		Antoine equation parameters, conversion factor (from mmHG to Pa): D=133.32
a	$\mathrm{m^{-1}}$	Specific surface area of the solid grains in the particle
c_p	$\mathrm{J\,kg^{-1}\,K^{-1}}$	Heat capacity
c	$\mathrm{kmol\,m^{-3}}$	Concentration
C	$\mathrm{m^{-1}}$	Constant for the calculation of the capillary pressure
D	$\mathrm{m^2\,s^{-1}}$	Molecular (binary) diffusion coefficient
h	$\mathrm{J\,kg^{-1}}$	Specific enthalpy
j^*	$\mathrm{kmol\,m^{-2}\,s^{-1}}$	Diffusive molar flux
K		Species permeability
l	m	Length
MW	$\mathrm{kg\,kmol^{-1}}$	Molecular weight of i
$\dot{n}$	$\mathrm{kmol\,m^{-2}\,s^{-1}}$	Molar flux
$NG/NL/NS/NR$		Total number of gas/liquid/solid species and reactions
p	Pa	Total pressure
p^*	Pa	Saturation pressure
$\dot{p}$	$\mathrm{kmol\,m^{-3}\,s^{-1}}$	Phase change rate of species i
$\dot{q}$	$\mathrm{W\,m^{-3}}$	Specific heat production rate (e.g., due to reaction)
r, r^*	m	Radial particle coordinate; normalized radial coordinate
R	$\mathrm{J\,kmol^{-1}K^{-1}}$	Universal gas constant (8314.41)
R	m	Outer particle radius
r_s	$\mathrm{kmol\,m^{-3}\,s^{-1}}$	Reaction rate per unit volume of porous solid
S		Pore saturation
s	$\mathrm{kmol\,m^{-3}\,s^{-1}}$	Chemical production rate per unit total volume
T	K	Temperature
V	$\mathrm{m^3}$	Volume
x		Mole fraction

1.2 Greek Characters

Variable	Unit	Meaning
α		Film breakage factor
α_s		Sintering factor
β	$\mathrm{m\,s^{-1}}$	Mass transfer coefficient
β	$\mathrm{m\,s^{-1}}$	Evaporation/drying rate constant
$\delta_{i,j}$		Kronecker delta function (=1 if $i = j$ and zero otherwise)
γ		Mass fraction of species i in the porous solids
γ	$\mathrm{N\,m^{-1}}$	Surface tension
ε		Phase fraction (volume-based)
$\nu_{i,j}$		Stoichiometric coefficient of species
ν		Kinematic viscosity
η	Pa s	Dynamic viscosity
τ		Tortuosity
λ	$\mathrm{W\,m^{-1}\,K^{-1}}$	Thermal conductivity
ρ	$\mathrm{kg\,m^{-3}}$	Density

1.3 Superscripts

Variable	Meaning
k	Spatial grid index
K	Knudsen
$conv$	Convective

1.4 Subscripts

Variable	Meaning
A	Apparent
i	Species index
c	Capillary
$g/l/s$	Gas/Liquid/Solid
$grain$	Grain
l, s	Liquid solvent
v	Evaporation
$react$	Reaction (e.g., heat of reaction)
0	Initial state
ij	Coefficient of i in j
eff	Effective value
$enviro$	Environment
$pore$	Pore
dry	Drying
w	Wall

2 Basic Approach and Scope

`ParScale` is designed to predict intra-particle fields (e.g., of the temperature) as a function of time and space. This documentation presents the underlying equations, details on simplifications made, and summarizes all numerical schemes used for spatial discretization.
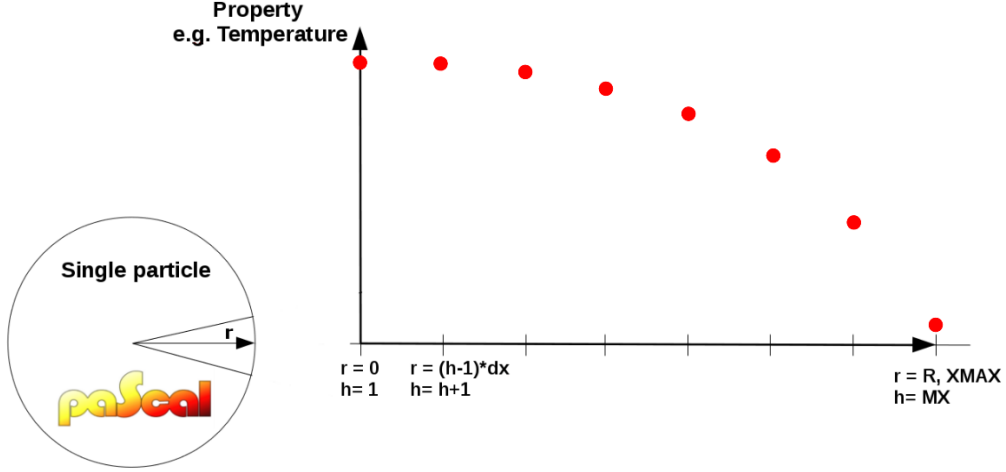
2.1 Overview

Figure 1: Overview of a typical solution that can be obtained with `ParScale` (e.g., temperature distribution within a spherical particle)

- The particle is discretized starting at $r = 0, h = 1$

- Every point coordinate until $h = MX$ ($MX=$ number of grid points to be set in input script using, e.g., `particle_mesh nGridPoints 20`) can be obtained using $r = (h-1) \cdot \triangle r$, with $\triangle r = \dfrac{R}{MX-1}$ with R being the outer particle radius.

- Discrete values of the intra-particle properties to be predicted (e.g., the temperature) are obtained by time-integration of the discretized equations, i.e., the so-called "Method of Lines" is used to solve the governing equations.

3 Governing Equations

In order to resolve temperature and species concentration profiles, balance equations for thermal energy and the local species concentration need to be established. The required closures (to solve these equations) models are presented in Section 4.

3.1 Thermal Energy Balance

The following equations represents the thermal energy balance:

$$\frac{\partial}{\partial t}\left(\sum_{i=1}^{NG}\varepsilon_g c_{g,i}h_{g,i}\,MW_i + \varepsilon_l c_{l,s}h_l\,MW_l + \rho_s h_s\right) \tag{1}$$

$$= \quad -\nabla\cdot\left(\sum_{i=1}^{NG}\dot{n}_{g,i}\,h_{g,i}\,MW_i + \alpha\,\dot{n}_{l,s}h_l\,MW_l - \lambda\frac{\partial T}{\partial r}\right) + \dot{q}_{react}$$

Replacing the enthalpy with the temperature times an average heat capacity, as well as taking the enthalpy of evaporation into acocunt, Eqn. (1) can be rewritten as

$$\frac{\partial}{\partial t}\left(\sum_{i=1}^{NG}\varepsilon_g c_{g,i}\,\triangle h_{v,i}\,MW_i\right) \tag{2}$$

$$+\quad \frac{\partial}{\partial t}\left(T\left[\sum_{i=1}^{NG}\varepsilon_g c_{g,i}\,MW_i\,c_{p,g,i} + \varepsilon_l c_{l,s}MW_l\,c_{p,l} + \rho_s c_{p,s}\right]\right)$$

$$=\quad -\nabla\cdot\left(\sum_{i=1}^{NG}\dot{n}_{g,i}\,\triangle h_{v,i}\,MW_i\right)$$

$$-\quad \nabla\cdot\left(T\left[\sum_{i=1}^{NG}\dot{n}_{g,i}MW_i\,c_{p,g,i} + \alpha\,\dot{n}_{l,s}\,MW_l\,c_{p,l}\right] - \lambda\frac{\partial T}{\partial r}\right)$$

$$+\quad \dot{q}_{react}$$

Taking the total gas balance equation into account, we get:

$$\frac{\partial}{\partial t}\left(T\left[\sum_{i=1}^{NG}\varepsilon_g c_{g,i}\,MW_i\,c_{p,g,i} + \varepsilon_l c_{l,s}MW_l\,c_{p,l} + \rho_s c_{p,s}\right]\right)$$

$$=-\quad \triangle h_{v,i}\sum_{i=1}^{NG}(\dot{p}_{g,i})$$

$$-\quad \nabla\cdot\left(T\left[\sum_{i=1}^{NG}\dot{n}_{g,i}MW_i\,c_{p,g,i} + \alpha\,\dot{n}_{l,s}\,MW_l\,c_{p,l}\right] - \lambda\frac{\partial T}{\partial}\right.$$

$$+\quad \dot{q}_{react}$$

3.2 Species Balance Equations

3.2.1 Solid Species

We assume that the change in the concentration of the solid is due to the rate of metal adsorption and a possible reaction, i.e., solids cannot diffuse and are also immobile otherwise. Therefore:

$$\frac{\partial}{\partial t} c_{s,i} = s_{s,i} + \dot{p}_{s,i} \tag{5}$$

Note, that there is no ε_s included on the left hand side of the equation since the unit of $c_{s,i}$ is in $\mathrm{kmol\,m_{tot}^{-3}}$.

3.2.2 Gas Species

The change of the concentration of gas species is expressed as the divergence of the molar flux, and possible source/sink terms due to reaction and phase change. Therefore:

$$\frac{\partial}{\partial t}(\varepsilon_g c_{g,i}) = -\nabla \cdot \dot{n}_{g,i} + s_{g,i} + \dot{p}_{g,i} \tag{6}$$

In this equation the gas flux $\dot{n}_{g,i}$ is the combined diffusive and convective flux. These fluxes are modelled as follows:

$$\dot{n}_{g,i} = \dot{n}_{g,i}^{[\mathrm{conv}]} + \dot{n}_{g,i}^{[diff]} \quad \text{with} \tag{7}$$

$$\dot{n}_{g,i}^{[\mathrm{conv}]} = x_i \dot{n}_g = \frac{c_{g,i}}{c_g} \dot{n}_g \quad \text{and} \tag{8}$$

$$\dot{n}_{g,i}^{[diff]} = -D_{g,i} \frac{\partial c_{g,i}}{\partial r} \tag{9}$$

3.2.3 Liquid Species

The formulation for the liquid species is in analogy to the gas species, with the only difference being that we take the film breakage factor α into account:

$$\frac{\partial}{\partial t}(\varepsilon_l c_{l,i}) = -\nabla \cdot (\alpha \dot{n}_{l,i}) + s_{l,i} + \dot{p}_{l,i} \tag{10}$$

3.3 Total Solid Balance

Since the units of the total solid concentration is in $\mathrm{kmol\,m_{tot}^{-3}}$, the following equation

$$\frac{\partial}{\partial t}\left(\varepsilon_s \frac{\overline{\rho}_s}{\overline{MW}_s}\right) = \sum_{i=1}^{NS} s_{s,i} + \sum_{i=1}^{NS} \dot{p}_{s,i} \tag{11}$$

can be used to calculate the total solid concentration. In addition, the phase fraction of the solid phase is expressed as:

$$\varepsilon_s = 1 - \varepsilon_l - \varepsilon_g. \tag{12}$$

3.4   Total Gas Balance

For the total gas equation we sum over all gas species balance equations to arrive at:

$$\frac{\partial}{\partial t}(\varepsilon_g c_g) = -\nabla \cdot \sum_{i=1}^{NG} \dot{n}_{g,i} + \sum_{i=1}^{NG}(s_{g,i} + \dot{p}_{g,i}). \tag{13}$$

By introducing the total gas flux (often referred to as 'drift flux') $\dot{n}_g$, we get

$$\frac{\partial}{\partial t}(\varepsilon_g c_g) + \nabla \cdot \dot{n}_g = \sum_{i=1}^{NG}(s_{g,i} + \dot{p}_{g,i}). \tag{14}$$

Applying the product rule for $\partial_t(\varepsilon_g c_g)$ leads to

$$\frac{\partial}{\partial t}(\varepsilon_g c_g) = \varepsilon_g \frac{\partial c_g}{\partial t} + c_g \frac{\partial \varepsilon_g}{\partial t} \quad \text{with} \tag{15}$$

$$\frac{\partial c_g}{\partial t} = \frac{\partial c_g}{\partial T}\frac{\partial T}{\partial t} + \frac{\partial c_g}{\partial p}\frac{\partial p}{\partial t}, \tag{16}$$

$$\frac{\partial c_g}{\partial T} = -\frac{p}{R\,T^2} \quad \text{(ideal gas law)}. \tag{17}$$

$$\tag{18}$$

Since we assume an isobaric system the pressure does not change over time. Therefore

$$\frac{\partial c_g}{\partial p}\frac{\partial p}{\partial t} = 0 \tag{19}$$

This allows us to back up the total gas flux from the change of the temperature, as well as the integral evaporation and reaction rate.

3.4.1   Total Gas Flow Rate

The total gas flux $\dot{n}_g$ from equation (14) is used to compute the total gas flow rate $\dot{N}_g$:

$$\dot{N}_g = A\,\dot{n}_g \tag{20}$$

$$\tag{21}$$

Thus, we get

$$\frac{\partial}{\partial t}(\varepsilon_g c_g) = -\nabla \cdot \left(\frac{\dot{N}_g}{A}\right) + \sum_{i=1}^{NG}(s_{g,i} + \dot{p}_{g,i}) \tag{22}$$

The total gas flow rate, and hence the total gas flux, can be calculated using:

$$\nabla \cdot \left(\frac{\dot{N}_g}{A}\right) = \sum_{i=1}^{NG}(s_{g,i} + \dot{p}_{g,i}) - \frac{\partial}{\partial t}(\varepsilon_g c_g). \tag{23}$$

4 Physical Models for Model Equations

4.1 Evaporation Rate

If a species evaporates, the phase change rate $\dot{p}_i$ (sometimes referred as drying rate $\dot{r}_{dry}$) has to be calculated. This phase change rate per unit surface are of the single is modeled with:

$$\dot{r}_{dry} = \frac{S(1-S)\,\beta\,\triangle c}{V_{tot}} \tag{24}$$

$$\dot{R}_{dry} = \frac{A_{pore}\,S(1-S)\,\beta\,\triangle c}{V_{tot}} \quad \text{with} \tag{25}$$

$$S = \frac{\varepsilon_l}{\varepsilon_g + \varepsilon_l}, \tag{26}$$

$$V_{tot} = \frac{l_{pore}\,r_{pore}^2\,\pi}{\varepsilon_g}, \tag{27}$$

$$A_{pore} = 2\pi\,l_{pore}\,r_{pore} \quad \text{and} \tag{28}$$

$$\triangle c = \frac{p_i^*}{R\,T} - c_i \tag{29}$$

where p_i^* is the saturation vapor pressure of species i at the local temperature. For the modeling of p^* the Antoine vapour pressure model is used [1].

4.1.1 Antoine Vapour Pressure Model

$$p^* = D\,10^{A - \frac{B}{C+T}} \tag{30}$$

Due to the conversion from [mmHG] to [Pa] D= 133.322. The equation parameters A,B,C depend on the species of interest.

4.2 Time Derivative of the Saturation Concentration

In order to calculate the heat of evaporation the time derivative of saturation concentration is needed and calculated as followed:

$$\frac{\partial c^*}{\partial t} = \frac{\partial}{\partial t}\frac{p^*}{R\,T} = \frac{1}{R\,T}10^{\left(A - \frac{B}{C+T}\right)} \tag{31}$$

$$= \underbrace{\frac{1}{R\,T}10^{\left(A - \frac{B}{C+T}\right)}}_{c^*}\left(\ln 10 - \frac{1}{T}\right) \tag{32}$$

4.3 Liquid flux

We assume that the convective liquid flux is following Darcys law [2]. Therefore:

$$N_{l,s} = -c_{l,s}\frac{K\,K_{l,eff}}{\nu_l}\,\bigtriangledown p_l \tag{33}$$

Here p_l is the liquid phase pressure which can be calculated with the gas phase pressure less the capillary pressure p_c:

$$\nabla p_l \;=\; p_g - p_c \quad \text{with} \tag{34}$$

$$p_c \;=\; 1.364 \cdot 10^5 \, \gamma \left(\frac{\varepsilon_l \, c_{l,s} \, MW_{l,s}}{\rho_s} \right)^{-0.63} \quad \text{modelled with} \tag{35}$$

$$p_c \;=\; C \, \gamma \, \varepsilon_l^{-0.63} \quad \text{with} \tag{36}$$

$$C = \text{const.} \;=\; 1.364 \cdot 10^5 \left(\frac{c_{l,s} \, MW_{l,s}}{\rho_s} \right)^{-0.63} \tag{37}$$

By assuming a constant solvent concentration $c_{l,s}$, it can be seen that C will stay constant for the calculation, and has to be specified as an input parameter by the user. Another possible model for the capillary pressure is [3]

$$p_c = 1.364 \cdot 10^5 \, \gamma \, (\varepsilon_l + 1.2 \cdot 10^{-4}). \tag{38}$$

The film breakage factor α (compare Eqn. (10)) ranges between 0 and 1 depending on the saturation (following definition in Eqn. (26)). The film breakage factor can be modelled as follows:

$$\alpha = 1 \quad \text{if} \quad S > \alpha_2 \tag{39}$$

$$\alpha = \frac{S - \alpha_1}{\alpha_2 - \alpha_1} \quad \text{if} \quad \alpha_2 > S > \alpha_1 \tag{40}$$

$$\alpha = 0 \quad \text{if} \quad S < \alpha_1 \tag{41}$$

Note that the user has to set α_1 and α_2 as input parameters.

5 Laplace Operator

Since `ParScale` is designed for calculating property profiles in different coordinate systems the following equations describe the Laplace operator in that systems.

5.1 Spherical Coordinates

$$\nabla \cdot [\,] \;\; = \;\; \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \, [\,] \right) \tag{42}$$

5.2 Cylindrical Coordinates

$$\nabla \cdot [\,] \;\; = \;\; \frac{1}{r} \frac{\partial}{\partial r} \left(r \, [\,] \right) \tag{43}$$

6 Numerics

6.1 Numerical approach

- CVODE is used for the discretization in time

  - CVODE features a 1 to 5th order (variable) backward differences scheme
  - CVODE features a variable step methods (i.e., CVODE will perform sub-time stepping to ensure a certain accuracy level)
  - CVODE has been proven to be a robust method, suitable for stiff systems of ODEs.

- The central differencing scheme (CDS, i.e., a second-order accurate scheme) has been chosen as the method for discretization in physical space

6.2 Discretization in Physical Space using CDS

$$\frac{\partial[\,]}{\partial r} = \frac{[\,]^{(k+1)} - [\,]^{(k-1)}}{2 \triangle r} + O(\triangle r^2) \tag{44}$$

$$\frac{\partial^2[\,]}{\partial r^2} = \frac{[\,]^{(k+1)} + [\,]^{(k-1)} - 2[\,]^{(k)}}{\triangle r^2} + O(\triangle r^2) \tag{45}$$

6.3 Discretization of Convective Fluxes

In the following the discretization of the convective transport terms are presented.

6.3.1 Thermal Energy Balance Equation

Assuming only convective transport the final equation for the discretization of the heat equation is:

$$
\begin{aligned}
\frac{\partial T^{(k)}}{\partial t} &= -\frac{2}{r^{(k)}} \left(\frac{\sum \dot{c}_p}{\bar{c}_{eff}\, \bar{c}_{p,eff}} \right)^{(k)} T^{(k)} \\
&\quad - \frac{1}{2 \triangle r} \left(\left[\frac{\sum \dot{c}_p}{\bar{c}_{eff}\, \bar{c}_{p,eff}} \right]^{(k+1)} T^{(k+1)} - \left[\frac{\sum \dot{c}_p}{\bar{c}_{eff}\, \bar{c}_{p,eff}} \right]^{(k-1)} T^{(k-1)} \right) \quad \text{with} \tag{46} \\
\sum \dot{c}_p &= \sum \dot{c}_p^{\text{conv}} \approx \dot{n}_g\, MW_g\, c_{p,g} + \dot{n}_l\, MW_l\, c_{p,l} \tag{47}
\end{aligned}
$$

6.3.2 Gas and Liquid Balance Equations

Since these two transport equations are very similar, in the following only the resulting equation is presented which account for the discretization of gas and liquid transport:

$$
\begin{aligned}
\frac{\partial c_{g/l,i}}{\partial t}^{(k)} &= -\frac{2}{r^{(k)}} \left(\frac{\dot{n}_{g,l}}{\varepsilon_g\, c_{g/l}} \right)^{(k)} c_{g/l,i}^{(k)} \\
&- \frac{1}{2\,\triangle\, r} \left(\left[\frac{\dot{n}_{g,l}}{\varepsilon_g\, c_{g/l}} \right]^{(k+1)} c_{g/l,i}^{(k+1)} - \left[\frac{\dot{n}_{g,l}}{\varepsilon_g\, c_{g/l}} \right]^{(k-1)} c_{g/l,i}^{(k-1)} \right)
\end{aligned} \tag{48}
$$

6.4 Discretization of Diffusive Fluxes

In the following the discretization of the diffusive transport terms are presented.

6.4.1 Heat Equation

$$
\begin{aligned}
\frac{\partial T}{\partial t} &= \frac{1}{r^2 \rho_{eff}\, c_{p,eff}} \left(\frac{\partial \lambda_{eff}}{\partial r} r^2 \frac{\partial T}{\partial r} + 2\,r\,\lambda_{eff} \frac{\partial T}{\partial r} + \lambda_{eff}\, r^2 \frac{\partial^2 T}{\partial r^2} \right) + \frac{\dot{q}_{react}}{\rho_{eff}\, c_{p,eff}} \tag{49} \\
&= \frac{1}{2\,\triangle\, r \rho_{eff}^k\, c_{p,eff}^k} \left(\frac{1}{2\,\triangle\, r} \left(\lambda^{k+1} - \lambda^{k-1} \right) \left(T^{k+1} - T^{k-1} \right) + \frac{2}{r^k} \lambda_{eff}^k \left(T^{k+1} - T^{k-1} \right) \right. \\
&+ \left. \frac{2}{\triangle r} \lambda_{eff} \left(T^{k+1} + T^{k-1} - 2T^k \right) \right) + \frac{\dot{q}_{react}}{\rho_{eff}^k\, c_{p,eff}^k} \tag{50}
\end{aligned}
$$

$$\tag{51}$$

6.4.2 Gas/Liquid Equation

The transport equation for the gas/liquid phase under the assumption of diffusive transport (compare Eqn. (7)) is:

$$
\begin{aligned}
\frac{\partial c_{g/l,i}}{\partial t} &= \frac{1}{r^2 \varepsilon_{g/l,i}} \left(\frac{\partial D_i}{\partial r} r^2 \frac{\partial c_{g/l,i}}{\partial r} + 2\,r\,D_i \frac{\partial c_{g/l,i}}{\partial r} + D_i\, r^2 \frac{\partial^2 c_{g/l,i}}{\partial r^2} \right) \tag{52} \\
&= \frac{1}{2\,\triangle\, r \varepsilon_{g/l,i}^k} \left(\frac{1}{2\,\triangle\, r} \left(D_i^{k+1} - D_i^{k-1} \right) \left(c_{g/l,i}^{k+1} - c_{g/l,i}^{k-1} \right) + \frac{2}{r^k} D_i^k \left(c_{g/l,i}^{k+1} - c_{g/l,i}^{k-1} \right) \right. \\
&+ \left. \frac{2}{\triangle r} D_i \left(c_{g/l,i}^{k+1} + c_{g/l,i}^{k-1} - 2c_{g/l,i}^k \right) \right) \tag{53}
\end{aligned}
$$

$$\tag{54}$$

6.5 Boundary Conditions

6.5.1 Middle of Sphere Heat Equation

Singularity in spherical coordinates at $r = 0$ appears by the assumption of symmetry. Therefore the first derivative of temperature after radius divided by radius is replaced by second derivative of temperature after radius (L'hopitals rule) which leads to

$$
\frac{\partial T}{\partial t} = \frac{\partial \lambda_{eff}}{\partial r} \frac{\partial T}{\partial r} + 3\,a_{eff} \frac{\partial^2 T}{\partial r^2}. \tag{55}
$$

11

$T^{(k-1)}$ results out of the *auxiliary point method*. At the middle of the sphere ($r = 0$) and under the assumption of symmetry ($T^{(k-1)} = T^{(k+1)}, \lambda_{eff}^{(k-1)} = \lambda_{eff}^{(k+1)}, D^{(k-1)} = D^{(k+1)}$) we get

$$\frac{\partial T}{\partial t} = 6\, a_{eff}\, \frac{T^{(k+1)} - T^{(k)}}{\triangle r^2} \quad \text{for } k = 0 \tag{56}$$

6.5.2 Middle of Sphere Gas/Liquid Equation Equation

In agreement with Eqn. (57) the boundary equation at the middle of the sphere for a gas or liquid species is:

$$\frac{\partial c_{g/l,i}}{\partial t} = 6\, \frac{D_i}{\varepsilon_{g/l,i}}\, \frac{c_{g/l,i}^{(k+1)} - c_{g/l,i}^{(k)}}{\triangle r^2} \quad \text{for } k = 0 \tag{57}$$

6.5.3 Boundary of Sphere

Three different boundary conditions are available in `ParScale` at the moment.

- Neumann

    - Fixed heat/species flux

    - Heat/Species flux is specified in [W] (or [kmol]) and will be imposed on the outer particle surface

    - Note that in the following eqn. $\dot{q}/\dot{j}^*$ is [W m^{-2}] or [kmol m^{-2}s^{-1}]

- Dirichlet

    - Fixed wall temperature or concentration

- Convective

    - Convective heat or mass transfer at the surface of the particle characterized with a transfer coefficient and a value for the surrounding fluid temperature (or concentration).

6.5.4 Neumann Boundary Condition

Note that the following equations are only valid for a heat transport. For mass transport simply replace

$$\dot{q} = j^* \tag{58}$$

$$\lambda_{eff} = D_i \tag{59}$$

$$T = c_{g/l,i} \tag{60}$$

$$a_{eff} = \frac{D_i}{c_{g/l,i}} \tag{61}$$

$$\dot{q} = -\lambda_{eff}\, \frac{\partial T}{\partial r} \tag{62}$$

$$T^{(k+1)} = T^{(k-1)} - \frac{2\,\dot{q}\,\triangle r}{\lambda_{eff}} \tag{63}$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{T^{(k-1)} - \dfrac{2\,\dot{q}\,\triangle r}{\lambda_{eff}} + T^{(k-1)} - 2\,T^{(k)}}{\triangle r^2} \tag{64}$$

$$= \frac{2\left(T^{(k-1)} - \dfrac{\dot{q}\,\triangle r}{\lambda_{eff}} - T^{(k)}\right)}{\triangle r^2} \tag{65}$$

$$\frac{\partial T}{\partial r} = \frac{T^{(k+1)} - \dfrac{2\,\dot{q}\,\triangle r}{\lambda_{eff}} - T^{(k-1)}}{2\,\triangle r} \quad \text{with} \;\; T^{(k-1)} = T^{(k+1)} \tag{66}$$

$$= -\frac{2\,\dot{q}\,\triangle r}{2\,\triangle r\lambda_{eff}} \tag{67}$$

$$= -\frac{\dot{q}}{\lambda_{eff}} \tag{68}$$

$$\frac{\partial T}{\partial t} = a_{eff} \cdot \left(\frac{2\left(T^{(k-1)} - \dfrac{\dot{q}\,\triangle r}{\lambda_{eff}} - T^{(k)}\right)}{\triangle r^2} - \frac{2\,\dot{q}}{R\,\lambda_{eff}}\right) \tag{69}$$

6.5.5 Dirichlet Boundary Condition

By setting the particle surface temperature/concentration to a fixed value we get:

$$T^{(k)}/c_{g/l,i}^{(k)} = T_w/c_w \tag{70}$$

6.5.6 Convective Boundary Condition

Note that the following equations are only valid for a heat transport. For mass transport simply replace

$$\dot{q} \;\; = \;\; j^* \tag{71}$$

$$\lambda_{eff} \;\; = \;\; D_i \tag{72}$$

$$T \;\; = \;\; c_{g/l,i} \tag{73}$$

$$a_{eff} \;\; = \;\; \frac{D_i}{c_{g/l,i}} \tag{74}$$

$$\alpha \;\; = \;\; \beta \tag{75}$$

$$\tag{76}$$

Assuming convective heat/mass transport:

$$\alpha \cdot (T^{(k)} - T^{(enviro)}) = -\lambda_{eff}\frac{\partial T}{\partial r} \tag{77}$$

- Calculation of *auxiliary point*

$$\alpha \cdot (T^{(k)} - T^{(enviro)}) = -\lambda_{eff}\frac{T^{(k+1)} - T^{(k-1)}}{2\,\triangle r} \tag{78}$$

with a grid Biot number

$$Bi_{\Delta r} = \frac{\alpha \, \triangle r}{\lambda_{eff}} \tag{79}$$

$$T^{(k+1)} = -2 \, Bi_{\Delta r} \left(T^{(h)} - T^{(enviro)} \right) + T^{(k-1)} \tag{80}$$

with $T^{(k+1)}$ at $r = R$

$$\frac{\partial T}{\partial t} = a_{eff} \cdot \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{R} \frac{\partial T}{\partial r} \right) \tag{81}$$

results in

$$
\begin{aligned}
\frac{\partial T}{\partial t} = & \frac{a_{eff}}{\triangle r^2} \left(- 2 \, Bi_{\Delta r} \left(T^{(k)} - T^{(enviro)} \right) + T^{(k-1)} + T^{(k-1)} - 2 \, T^{(k)} \right) + \\
& \frac{2 \, a_{eff}}{2 \, R \, \triangle r} \left(- 2 \, Bi_{\Delta r} \left(T^{(k)} - T^{(enviro)} \right) + T^{(k-1)} - T^{(k-1)} \right)
\end{aligned}
\tag{82}
$$

$$
\begin{aligned}
\frac{\partial T}{\partial t} = & \frac{2 \, a_{eff}}{\triangle r^2} \left(- Bi_{\Delta r} \left(T^{(k)} - T^{(enviro)} \right) + T^{(k-1)} - T^{(k)} \right) + \\
& \frac{a_{eff}}{R \, \triangle r} \left(- 2 \, Bi_{\Delta r} \left(T^{(k)} - T^{(enviro)} \right) \right)
\end{aligned}
\tag{83}
$$

If a heat/species flux from `LIGGGHTS` is pulled trough a coupling model it acts as a thermal source term and is added for the outer grid point.

References

[1] Johann C Wurzenberger, Susanne Wallner, Harald Raupenstrauch, A Graz, and Johannes G Khinast. Thermal Conversion of Biomass : Comprehensive Reactor and Particle Modeling. 48(10), 2002.

[2] Xue Liu, Johannes G Khinast, and Benjamin J Glasser. Drying of supported catalysts for low melting point precursors : Impact of metal loading and drying methods on the metal distribution. *Chemical Engineering Science*, 79:187–199, 2012.

[3] Azzeddine Lekhal, Benjamin J. Glasser, and Johannes G. Khinast. Impact of drying on the catalyst profile in supported impregnation catalysts. *Chemical Engineering Science*, 56(15):4473–4487, 2001.