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A stochastic differential equation
approach to grain-particle surface
reactions, in particular $\text{H} + \text{H} \rightarrow \text{H}_2$.

Bachelorscriptie, October 12, 2011

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1 Introduction

Astrochemistry is the branch of astronomy that deals with the detection of molecules and elements in the universe. The observation of the molecule is done by making a spectrum of an object. Then the features in the spectrum are analysed for known bands and spectral lines. The unknown features in the spectrum can not be identified without making an educated guess about the type of molecules that can be found in the specific region of space. That type of molecule is then tested in a laboratory for making the same spectral lines. If the molecule exhibits a spectrum that can be found in the spectrum of the observation, then it is very likely that this molecule is responsible for the observed spectral features.

Astrochemistry does have some problems that cannot be overcome easily. The boundary conditions of the laboratory experiment deviates from the conditions of the observed region. Not in the last place because of the great difference in pressure and density. To overcome this problem astrochemical models were developed to interpret the results of the laboratory to the conditions of the observed region. With this dataset it is now possible to compare unbiased with the observed spectrum. If a match is found then it is highly likely that the molecule or element is responsible for the spectral features. It is not always possible to identify a single molecule to a certain spectral feature because several molecules have spectral lines very close to each other. Therefore the resolution can cause the spectral lines to be the same. Identification is thus done with great care.

Hydrogen is the most abundant element in the universe. The element is very important in many processes, because the molecule is a coolant, a shielder of UV radiation and a precursor of many molecules. The theory of the Big Bang predicts that hydrogen was solely created in the atomic form. Molecular hydrogen, H_2 , was not formed at that time. Today molecular hydrogen can be found in the universe. Collisions of gas molecules of hydrogen cannot account for the molecular hydrogen in cold, low density regions of the universe. To form molecular hydrogen in the gas phase two atoms of hydrogen would have to collide and send out a photon for the excess energy. Because the release of a photon during this formation is slow, it is very unlikely to form molecular hydrogen out of the collision of two gas-phase hydrogen atoms. Another way would be through a three-body collision, where the third body takes up the excess energy. Three body collisions do however not occur in the low density regions of space.

The general consensus about the origin of the high abundance is the formation of molecular hydrogen at the surfaces of dust particles. (Chang et al., 2004) The energy surplus of the formation is transferred to the surface of the dust particle. This allows for a much higher probability of forming molecular hydrogen. There are two major mechanisms for this reaction. The first, a gas phase hydrogen atom reacts with another hydrogen atom that is bound to the surface of the dust particle at a fixed position. This mechanism is known as Eley-Rideal (Chang et al., 2004). In the second, two hydrogen atoms are bound loosely to the surface. This allows atoms to diffuse across the surface. This mechanism is

known as Langmuir-Hinshelwood. (Chang et al. 2004) We are interested in the latter mechanism.

The conditions under which these molecules form are diverse in terms of density, temperature and radiation field. All these conditions have a severe influence on the formation rate of molecules. The radiation field can split H_2 into H atoms. The temperature influences the desorption and the diffusion rate according to

$$R_{\text{hop}} = \nu e^{\left(-\frac{E_{\text{hop}}}{k_{\text{B}}T}\right)} \quad (1)$$

with ν the vibrational frequency, E the activation energy for either desorption or diffusion, k_{B} the Boltzmann constant, and T the temperature of the surface in Kelvin. The density influences the rate per unit volume with which the atoms impinge on the grain surface:

$$R_{\text{acc,H}} = \frac{1}{2}\rho_{\text{H}}v_{\text{H}}\sigma\gamma\rho_g \quad (2)$$

with ρ_{H} the number density of H atoms in the gas phase, v_{H} the speed of H atoms in the gas phase, σ the average cross-sectional area of a grain, γ the fraction of H atoms striking the grain that eventually form a molecule and ρ_g the number density of dust grains. (Biham et al., 2005)

Grain chemistry models have been constructed to follow the formation of molecules in time. As mentioned the physical conditions have a substantial influence on the formation, but also on the accuracy of the grain chemistry models. Models for high density break down at low density, while low density models are computationally too expensive for high densities. High density models break down in the low density region because of the statistical interpretation of the number of particles on the surface of a dust particle (Lohmar et al, 2009). The total number of particles on the surface is a sum of the indicators indicating that a location is occupied or not. Of the individual atoms this cannot be determined. Therefore the number of particles on the surface is a stochastic variable. In the high density limit this variable is subject to the law of large numbers and implies that the deviations with respect to the mean are very small. In the low density limit the deviations are not small and can even be larger than the mean. Therefore a model for the high density region is still very accurate when it neglects the deviations, but in the low density region it is not accurate any more. A larger problem is the use of the square of the mean of the number of particles on the grain to approximate the second moment of the number of particles on the grain. The difference is the variance of the number of particles on the grain. Only when the variance is negligible next to the square mean of the number of particles it is allowed to use this approximation. Therefore the model of the high density region is called a model in the stochastic region. The low density model has to incorporate the probability density function of the position and the extreme deviations from the mean. Thus the model must describe the behaviour very precise. Therefore the model is called a model of the deterministic region.

In the intermediate region it is difficult to evaluate the models. Therefore a new model is needed for the intermediate region. If the model is correct, than it

coincides in the low density region with the computationally expensive model, while in the high density region it coincides with the model for that region. The validation of the model in the intermediate region can be done for the formation of molecular hydrogen because the low density model and the high density model are still valid in this region and coincide with each other.

2 Goal of the Bachelor Research Project

In the previous section it was outlined why an intermediate region astrochemistry grain model is necessary. It was also argued why other models have problems with this region. To overcome these problems we have set the following goal:

Goal: *To mathematically determine whether a model can be made such that it satisfies the following conditions and if so to create such a model.*

- 1. consistent in both the deterministic and the stochastic region*
- 2. stable towards different densities of H-gas*
- 3. computational order is low (polynomial, polynomial with low degree, exponential with low exponent)*
- 4. retains continuous rate equations in limit of large numbers*

3 Rate and Modified Rate equations

In the late 18th century the gas hydrogen was found as an indivisible substance. It became clear that it must be an elementary substance. With such gasses it was possible to do reactions in a way not possible before. In those reactions people found empiric relationships for the formation of substances. Today these relationships are called the rate equations. These equations were used to calculate and predict quantities of substances forming in gas phase. Therefore it is a deterministic model. When people found out that gasses contains almost an uncountable amount of particles per cubic meter it became clear that the model only worked that well because of the central limit theorem. Thus for low amounts of particles per cubic meter it is possible that the rate equations do not agree any more. Therefore modified rate equations were needed. This model has been used to accommodate the problems in the stochastic regime.

Rate equations are a system of differential equations to describe a chemical reaction macroscopically. Normal rate equations use the expectation of the number of particles just as the modified rate equations uses the expectation of the number of particles. But rate equations was historically defined with the actual number of particles. This difference is subtle. Historically the rate equations implementation assumes that the kinematics of the particles are governed by these equations, while the rate equations method of today assumes that the kinematics of the particles are governed by a number density function, which has an expectancy that is governed by the historical rate equations. Modified rate equations is not different than rate equations with respect to the assumptions on the kinematics of particles. The difference between them are a few modifications that are based on the particle of the species such that the validity is in a longer range.

The rate equations have been very successful in calculations because of a few properties. The rate equations have originally been derived for gas phase species. Thus the solution of the rate equations are easy to couple to the gas phase rate equations. Secondly the use of a differential equation per species makes the computation not expensive, especially if the differential equations are uncoupled. Thus a simulation can be made very accurate or a lot of different boundary conditions can be simulated.

3.1 Rate equations

The rate equations are a set of differential equations to describe a chemical reaction macroscopically, as mentioned above. It is an empirical relationship that can be theoretically derived for the region in which the law of large numbers can be applied on both the density as the change of the density, also known as the deterministic region.

When N_H is the number of molecules of atomic hydrogen on the grain surface and N_{H_2} is the number of molecules of molecular hydrogen on the grain surface, the standard rate equations for the formation of molecular hydrogen

can be given as the system of two differential equations

$$\begin{aligned}\frac{dN_{\text{H}}}{dt} &= R_{\text{acc,H}} - R_{\text{hop,H}}N_{\text{H}} - 2R_{\text{hop,H}}\frac{\kappa_{\text{HH}}}{S}N_{\text{H}}^2 \\ &= F_{\text{H}} - W_{\text{H}}N_{\text{H}} - 2A_{\text{H}}N_{\text{H}}^2\end{aligned}\quad (3)$$

and

$$\begin{aligned}\frac{dN_{\text{H}_2}}{dt} &= R_{\text{acc,H}_2} - R_{\text{hop,H}_2}N_{\text{H}_2} + \mu R_{\text{hop,H}}\frac{\kappa_{\text{HH}}}{S}N_{\text{H}}^2 \\ &= F_{\text{H}_2} - W_{\text{H}_2}N_{\text{H}_2} + \mu A_{\text{H}}N_{\text{H}}^2\end{aligned}\quad (4)$$

with F_i the external flux of the species i , E_b the desorption/binding energy, E_D the diffusion energy, k_{B} the Boltzmann constant, μ the fraction of H_2 molecules attaching to the surface, S the number of sites on the grain, κ_{HH} the diffusion rate and $R_{\text{hop},i}$ is (1) with a species i specific energy E .

The differential equations consists of terms representing processes like adsorption, desorption and diffusion leading to the actual reaction. The F_i terms are flux terms that represent the adsorption of molecules by the grain surface. The W_iN_i term represents the desorption of species i from the grain surface. The $A_{\text{H}}N_{\text{H}}^2$ terms represent the actual reaction at the surface. All these terms can be physically explained. The adsorption term has no N_{H} term in it, because it is independent of the number of molecules on the grain surface. It is only determined by the density of molecules of the species in the direct neighbourhood of the grain. The desorption term is linear in N_{H} because every molecule on the grain has a probability to desorb and thus the total desorption in this macroscopic limit is equal to the expectancy, which is equal to the probability of desorption times the number of molecules.

The reaction term is a quadratic one, because every combination of two atoms on the grain surface can react with each other because of reaction after diffusion every couple of identical atoms have a positive meeting probability. Fundamental set theory now gives the quadratic dependency. The efficiency of the reaction is then defined as

$$\eta = \frac{2R_{\text{H}_2}}{F_{\text{H}}}\quad (5)$$

with

$$R_{\text{H}_2} = W_{\text{H}_2}N_{\text{H}_2} + (1 - \mu) A_{\text{H}}N_{\text{H}}^2 - F_{\text{H}_2}.\quad (6)$$

3.2 Modified rate equations

The modified rate equation differ from the ordinary rate equation in several modifications and interpretations. Modifying the rate equations in this way makes the rate equations valid in a larger domain. In the rate equations a process like the reaction is seen as a process that incorporates two adsorptions, diffusion and the reaction itself as one term, while in the modified rate equations the terms are viewed as independent processes. The adsorption is governed by the flux, thus the reaction is ultimately limited by the flux and therefore the flux should not be incorporated into the reaction term. This difference makes

the modified rate equation easier to modify to receive a larger validity domain than the ordinary rate equations.

One of the first modifications is the application of the boundary condition for every modified rate equation, which is the continuity threshold. The change from rate to modified rate must be a continuous change. Without any modification there is no guarantee that the change from modified rate to ordinary rate equations is continuous. A solution for this problem can be the introduction of a fraction function f . This function gives the fraction of particles that has to be modelled with modified rate equations. The other part has to be modelled with normal rate equations. The final system is thus a linear combination between (1) and (1) modified & (2) and (2) modified (Garrod 2008). A possible function f is the function $\frac{1}{((N_{\text{H}})+1)((N_{\text{H}_2})+1)}$.

The second modification is the modification for at the low density part of the stochastic region. In this part of the region the quadratic term is not valid any more. The quadratic term was received by fundamental set theory. The assumption was that in the stochastic region deviations of one are negligible. In the low density part of the stochastic region this is not valid any more. According to set theory the number of unique combinations of Z particles out of a set of $Y \geq Z$ identical particles is equal to

$$\binom{Y}{Z} = \frac{Y!}{Z!(Y-Z)!} = \frac{Y(Y-1)(Y-2)\dots(Y-(Z-1))}{Z(Z-1)\dots 1}. \quad (7)$$

Applying this to the formation H_2 we get Y equal to N_{H} and Z is equal to 2. The number of combinations is therefore $\frac{1}{2}N_{\text{H}}(N_{\text{H}}-1)$. Modifying N_{H}^2 into $N_{\text{H}}(N_{\text{H}}-1)$ makes the (modified) rate equation valid for this part of the stochastic region (Lohmar et al. 2009). Note that the factor of half was already incorporated in the coefficient.

The third modification that should be considered is a modification for (modified) rate equations is grain site occupation. The differential equations are based on the number of particles on the grain. The driving force of the equations are the terms F_{H_i} . These terms are the terms of adsorption. Thus particles from the gas attach to the grain. This implies that there exists a free grain site. This is normally assumed, but in the high density part of the stochastic region this is certainly not the case. Therefore there should be a correction for this. The appropriate correction is a factor $\max\left(\frac{S-N_{\text{H}}-N_{\text{H}_2}}{S}, 0\right)$ for F_i . This correction breaks down when more than one adsorption term is corrected in the same way, then competition between reactions can occur (Garrod, 2008). Normally the competition is discarded or is already incorporated in the terms and do not need further explanation. In the same way the quadratic term can be corrected for free grain sites.

In figure 1 it is showed how quantitatively the modified rate equations differ from the normal rate equations.

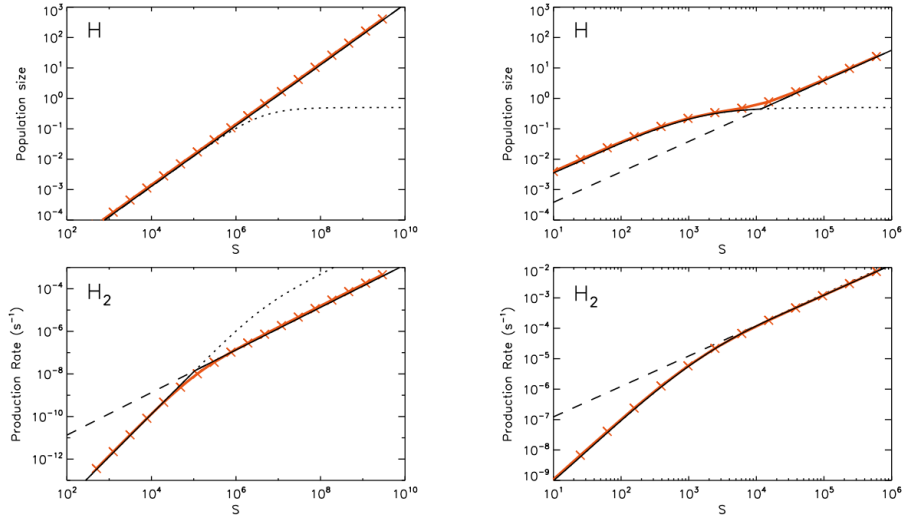


Figure 1: Population of H atoms and production rate of H_2 on grain surface as a function of S , the number of sites per grain with (left) low flux and (right) high flux. Solid black lines indicate the modified rate equations with the second modification. The dashed lines are the standard rate equations. The dotted lines are not important and the red lines are the results of the master equation, which will be explained in the next section. Picture from Garrod, 2008.

As can be seen from figure 1 around $S = 10^5$ for low flux and $S = 10^4$ for high flux there exists a turning point. Above this value the modified rate equations behaves like the normal rate equations, while below this value there exists a large deviation. The validity of this change cannot be done at this moment. When the master equations is explained it should be possible to address the problem of validity.

4 Master Equation

The master equation approach is the approach in which one modifies the rate equations by explicitly writing out the terms of the differential equations for every value of $\mathbb{P}(N_H)$, the probability density function with respect to the number of atomic hydrogen particles on the surface grain, and $\mathbb{P}(N_{H_2})$, the probability density function with respect to the number of molecular hydrogen particles on the surface grain. Since the discrete aspect is used in this approach, is this approach valid in the stochastic regime. The approach will give two differential equations

$$\begin{aligned}
\frac{d\mathbb{P}(N_H)}{dt} &= R_{\text{acc,H}} [\mathbb{P}(N_H - 1) - \mathbb{P}(N_H)] \\
&\quad - R_{\text{hop,H}} [N_H \mathbb{P}(N_H) - (N_H + 1) \mathbb{P}(N_H + 1)] \\
&\quad - R_{\text{hop,H}} \frac{\kappa_{\text{HH}}}{S} \left[N_H (N_H - 1) \mathbb{P}(N_H) \right. \\
&\quad \quad \left. - (N_H + 1) (N_H + 2) \mathbb{P}(N_H + 2) \right] \\
&= F_H [\mathbb{P}(N_H - 1) - \mathbb{P}(N_H)] \\
&\quad - W_H [N_H \mathbb{P}(N_H) - (N_H + 1) \mathbb{P}(N_H + 1)] \\
&\quad - A_H \left[N_H (N_H - 1) \mathbb{P}(N_H) \right. \\
&\quad \quad \left. - (N_H + 1) (N_H + 2) \mathbb{P}(N_H + 2) \right] \tag{8}
\end{aligned}$$

$$\begin{aligned}
\frac{d\mathbb{P}(N_{H_2})}{dt} &= R_{\text{acc,H}_2} [\mathbb{P}(N_{H_2} - 1) - \mathbb{P}(N_{H_2})] \\
&\quad - R_{\text{hop,H}_2} [N_{H_2} \mathbb{P}(N_{H_2}) - (N_{H_2} + 1) \mathbb{P}(N_{H_2} + 1)] \\
&\quad + \mu R_{\text{hop,H}} \frac{\kappa_{\text{HH}}}{S} \langle N_H (N_H - 1) \rangle [\mathbb{P}(N_{H_2} - 1) - \mathbb{P}(N_{H_2})] \\
&= F_{H_2} [\mathbb{P}(N_{H_2} - 1) - \mathbb{P}(N_{H_2})] \\
&\quad - W_{H_2} [N_{H_2} \mathbb{P}(N_{H_2}) - (N_{H_2} + 1) \mathbb{P}(N_{H_2} + 1)] \\
&\quad + \mu A_H \langle N_H (N_H - 1) \rangle [\mathbb{P}(N_{H_2} - 1) - \mathbb{P}(N_{H_2})] \tag{9}
\end{aligned}$$

with the variables and constants as specified in the previous section (Biham et al., 2005).

The $F_H [\mathbb{P}(N_H - 1) - \mathbb{P}(N_H)]$ term is the adsorption term for adsorption of one atom with a specified flux F_H . The $W_H [N_H \mathbb{P}(N_H) - (N_H + 1) \mathbb{P}(N_H + 1)]$ term is the desorption term for desorption of one atom with desorption flux W_H . The $A_H [N_H (N_H - 1) \mathbb{P}(N_H) - (N_H + 1) (N_H + 2) \mathbb{P}(N_H + 2)]$ term is the reaction term of the reaction $H + H \rightarrow H_2$.

For the second differential equation all these terms have the same meaning. Only the $\mu A_H \langle N_H (N_H - 1) \rangle [\mathbb{P}(N_{H_2} - 1) - \mathbb{P}(N_{H_2})]$, reaction term for H_2 is different, because the $\langle N_H (N_H - 1) \rangle$ term is the expectation of the number of combinations of two atomic hydrogen particles reacting. The use of expectation was necessary for decoupling of the differential equations, otherwise the joint distribution function was needed. The reaction of two H to one H_2 is such that any increase in N_{H_2} must be equal to one. Therefore the $[\mathbb{P}(N_{H_2} - 1) - \mathbb{P}(N_{H_2})]$ factor in the reaction term of H_2 is necessary. The $\mu A_H \langle N_H (N_H - 1) \rangle$ factor is the speed with which the probability having N_{H_2}

4.1 Boundary conditions

A boundary condition of this approach is the demand that the approach has to agree with the macroscopic limit: the rate equations. This can be shown in a

very simple way:

$$\begin{aligned}
\frac{d\langle N_H \rangle}{dt} &= \frac{d \sum_{N_H=0}^{\infty} N_H \mathbb{P}(N_H)}{dt} \\
&= \sum_{N_H=0}^{\infty} N_H \frac{d\mathbb{P}(N_H)}{dt} \\
&= \sum_{N_H=0}^{\infty} N_H F_H [\mathbb{P}(N_H - 1) - \mathbb{P}(N_H)] \\
&\quad - \sum_{N_H=0}^{\infty} N_H W_H [N_H \mathbb{P}(N_H) - (N_H + 1) \mathbb{P}(N_H + 1)] \\
&\quad - \sum_{N_H=0}^{\infty} N_H A_H [N_H (N_H - 1) \mathbb{P}(N_H) \\
&\quad - (N_H + 1)(N_H + 2) \mathbb{P}(N_H + 2)] \\
&= \sum_{N_H=0}^{\infty} F_H [(N_H + 1) \mathbb{P}(N_H) - N_H \mathbb{P}(N_H)] \\
&\quad - \sum_{N_H=0}^{\infty} W_H [N_H^2 \mathbb{P}(N_H) - N_H (N_H - 1) \mathbb{P}(N_H)] \\
&\quad - \sum_{N_H=0}^{\infty} A_H \left[(2N_H)^2 (2N_H - 1) \mathbb{P}(2N_H) \right. \\
&\quad \left. - (2N_H - 2) \cdot 2N_H (2N_H - 1) \mathbb{P}(2N_H) \right] \\
&\quad - \sum_{N_H=0}^{\infty} A_H \left[(2N_H + 1)^2 (2N_H) \mathbb{P}(2N_H + 1) \right. \\
&\quad \left. - (2N_H - 1) \cdot 2N_H (2N_H + 1) \mathbb{P}(2N_H + 1) \right] \\
&= F_H \sum_{N_H=0}^{\infty} \mathbb{P}(N_H) - W_H \sum_{N_H=0}^{\infty} N_H \mathbb{P}(N_H) \\
&\quad - 2A_H \sum_{N_H=0}^{\infty} (2N_H) (2N_H - 1) \mathbb{P}(2N_H) \\
&\quad - 2A_H \sum_{N_H=0}^{\infty} (2N_H + 1) (2N_H) \mathbb{P}(2N_H + 1) \\
&= F_H - W_H \langle N_H \rangle - 2A_H \langle N_H (N_H - 1) \rangle \tag{10}
\end{aligned}$$

This will be analogue for the second differential equation.

Because $\langle N_H (N_H - 1) \rangle \approx \langle N_H^2 \rangle$ holds in the asymptotic limit, it is thus proven that for the expectancies of N_H, N_{H_2} the master equations will asymptotically converge to the modified rate equations. Thus using the central limit theorem it is proven that the master equations will asymptotically converge to the normal rate equations.

Therefore the master equation method is allowed to be used as a more correct variant of the rate equations in the deterministic region.

This method is correct, but impracticable. The correct method requires to calculate all the time-dependent probability functions. Thus it would require an infinite amount of differential equations to be solved. This is either not easy to do with mathematical tricks for infinitely large matrices or it is impossible to

do on a computer. A good approximation assumes that the probabilities of N_{H_i} deviating very much from the mean N_{H_i} are negligible. A better master equation approach would use a joint probability density function of N_H and N_{H_2} and then calculate the marginals.

The master equation can only be validated with either an experiment in a laboratory or interstellar research. The second is impossible due to the unknown spectral lines for the specific molecules at this density and pressure. The first is impossible due to the present day technical capabilities. In laboratories the pressure and the density is still magnitudes too high, therefore it is not possible to get the correct values. It could be possible to simulate the particles and the grain to simulate the reaction. However this is not computational possible due to the high amount of particles needed for a calculation of this kind. It is possible to compare the master equation with the rate and modified rate equations. In figure 1 it is possible to compare the master equation with the modified rate equation and in figure 2 it is possible to compare it with the normal rate equation. But these comparisons assume that if the results match in a certain region that the results of an other region is correct as well. But this assertion can not be validated with direct evidence.

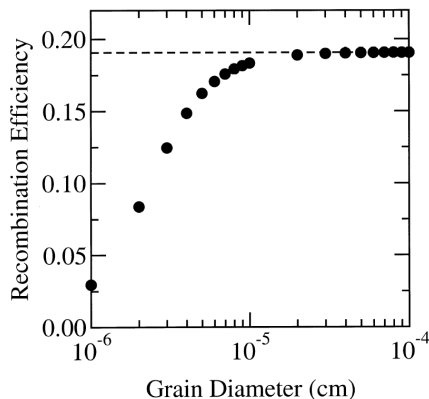


Figure 2: Population of H atoms and production rate of H_2 on grain surface as a function of S , the number of sites per grain. Solid black circles indicate the master equation. The dashed line is the standard rate equations. Picture from Biham et al., 2005.

In figure 1 it can be seen that the modified rate equations and the master equations give almost identical answers. This implies that the transition of deterministic to stochastic regime is can be very good modelled with the master equations and the modified rate equations. Thus the modified rate equation can be validated provided that the master equation is correct. Figure 2 show just like can be seen in figure 1 that the normal rate equation equations differs very much from the master equation for grains smaller than a certain grainsize. Above this size the two models coincide.

5 First Model

We attempt to create a model that is correct for the intermediate regime. To do this we will use several elements from both the master equation and the rate equations. The idea behind the models is the fact that the master equations and the rate equations are a consequence of the continuous movement of a particle. Therefore all the processes are defined in terms of the components of the position of the particles. The description of the processes will be based on the description of rate equations.

5.1 Naive model

The model is based on the rate equations with the addition of a random walk for the positions of the molecules. The details of the model are based on the discreteness of the increments, discreteness of the particles and on the physical grounds that particle positions are random walks, when time is made discrete. We assume that the random walks are Brownian motion, justified by the fact that in the limit of the time step size, proportional to the position step size, going to zero a discrete random walk on a lattice will become Brownian motion. This assumption is reasonable, because it assumes a constant speed of a particle.

Before we can propose our model we first introduce the naive differential equations based on the random walk of a particle (not necessarily Brownian motion), the rate equations and the discreteness of the particles

$$\begin{aligned} \frac{dN_H}{dt} &= \sum_{i=1}^n F_H \delta(iZ_t) \mathbf{1}_{\{\frac{d_i Z_t}{dt} < 0\}} - \sum_{i=1}^n W_H \delta(iZ_t) \mathbf{1}_{\{\frac{d_i Z_t}{dt} > 0\}} \\ &\quad - \sum_{i=1}^n \sum_{j < i} A_H \delta(iZ_t) \delta(jZ_t) \delta\left({}_j \vec{X}_t - {}_i \vec{X}_t\right) \times \\ &\quad \times \delta\left(\frac{d_i Z_t}{dt}\right) \delta\left(\frac{d_j Z_t}{dt}\right) \end{aligned} \quad (11)$$

$$\begin{aligned} \frac{dN_{H_2}}{dt} &= F_{H_2} - W_{H_2} N_{H_2} \\ &\quad + \sum_{i=1}^n \sum_{j < i} \mu A_H \delta(iZ_t) \delta(jZ_t) \delta\left({}_i \vec{X}_t - {}_j \vec{X}_t\right) \times \\ &\quad \times \delta\left(\frac{d_i Z_t}{dt}\right) \delta\left(\frac{d_j Z_t}{dt}\right) \end{aligned} \quad (12)$$

$${}_i \vec{X}_t = ({}_i X_{t,i}, {}_i Y_{t,i}, Z_t) \quad (13)$$

$$N_H = \sum_{i=1}^n \delta(iZ_t) \delta\left(\frac{d_i Z_t}{dt}\right) \quad (14)$$

with F_H, W_H, A_H constants defined previous, ${}_i X_{t,i}, {}_i Y_{t,i}, Z_t$ are three independent one-dimensional random walks of the i -th molecule of atomic hydrogen

H, $\mathbf{1}_{\{\text{condition}\}}$ is an indicator function of the specified condition, which means that the indicator is equal to a positive constant when the condition is true, otherwise its equal to 0 and the integral over the indicator is equal to c times the size (measure) of the condition. The Dirac delta function $\delta(x - a)$ is also an indicator function but the condition is a point in the real line, c equals ∞ and the integral equals 1. Therefore it is a special kind of indicator function.

The $\sum_{i=1}^n F_H \delta(iZ_t) \mathbf{1}_{\{\frac{d_i Z_t}{dt} < 0\}}$ term is the adsorption term and corresponds to the F_H terms. The term $\delta(iZ_t) \mathbf{1}_{\{\frac{d_i Z_t}{dt} < 0\}}$ causes the particle to arrive on the grain, which is assumed to be $Z = 0$.

The $\sum_{i=1}^n W_H \delta(iZ_t) \mathbf{1}_{\{\frac{d_i Z_t}{dt} > 0\}}$ term is the desorption term and corresponds to $W_H N_H$. The term $\mathbf{1}_{\{\frac{d_i Z_t}{dt} > 0\}}$ is needed to have only the desorbing molecules.

The term $\delta(iZ_t)$ causes an increase of one per particle on the grain per time step. Thus this term corresponds to the N_H factor.

The term $\sum_{i=1}^n \sum_{j < i} A_H \delta(iZ_t) \delta(jZ_t) \delta(i\vec{X}_t - j\vec{X}_t) \delta\left(\frac{d_i Z_t}{dt}\right) \delta\left(\frac{d_j Z_t}{dt}\right)$ corresponds to $A_H N_H (N_H - 1)$. The term $\delta(iZ_t) \delta(jZ_t)$ causes in the high density limit the use of combinations of possible reacting particles, which is an amount corresponding to $\frac{1}{2} N_H (N_H - 1)$. The term $\delta(i\vec{X}_t - j\vec{X}_t)$ causes particles to react when they are on the same position. The term $\delta\left(\frac{d_i Z_t}{dt}\right) \delta\left(\frac{d_j Z_t}{dt}\right)$ causes the reacting particles to stay on the grain.

5.2 Voluminous particle model

In the naive particle model we did not take into account that for chemical processes an atom has a finite mean square radius of the orbit of an electron. Thus using the atoms as point sources is not sufficient.

We can change this by replacing the point positions, that give rise to delta functions, to volumes, that give rise to normal indicator functions. Besides this change we also have to change the notion of identical position. For a process it is not necessary to demand only a point position for a particle to start the process. It is sufficient to start a process if the particle is in the influence radius of the process. Thus adsorption when the particle close enough to the surface, reaction when two particles are close enough. Therefore the surface can be modelled using a centerheight at every position such that more complex surfaces can be modelled. Implementing these changes into the model we get the model

$$\begin{aligned} \frac{dN_H}{dt} &= \sum_{i=1}^n \mathbf{1}_{\{|iZ_t - \pi| < \sigma\}} \left[F_H \mathbf{1}_{\{\frac{d_i Z_t}{dt} < 0\}} - W_H \mathbf{1}_{\{\frac{d_i Z_t}{dt} > 0\}} \right] \\ &\quad - 2 \sum_{i=1}^n \sum_{j < i} A_H \left[\mathbf{1}_{\{|iZ_t - \pi| < \sigma\}} \mathbf{1}_{\{|jZ_t - \pi| < \sigma\}} \mathbf{1}_{\{||j\vec{X}_t - i\vec{X}_t|| < \rho\}} \right] \\ &\quad \times \delta\left(\frac{d_i Z_t}{dt}\right) \delta\left(\frac{d_j Z_t}{dt}\right) \end{aligned} \quad (15)$$

$$\frac{dN_{H_2}}{dt} = F_{H_2} - W_{H_2} N_{H_2}$$

$$\begin{aligned}
& + \sum_{i=1}^n \sum_{j < i} A_H \left(\mathbf{1}_{\{|_i Z_t - \pi| < \sigma\}} \mathbf{1}_{\{|_j Z_t - \pi| < \sigma\}} \mathbf{1}_{\{||_i \vec{X}_t - _j \vec{X}_t|| < \rho\}} \right. \\
& \left. \times \delta \left(\frac{d_i Z_t}{dt} \right) \delta \left(\frac{d_j Z_t}{dt} \right) \right] \quad (16)
\end{aligned}$$

$${}_i \vec{X}_t = ({}_i X_{t,i} \ Y_{t,i} \ Z_t) \quad (17)$$

$$N_H = \sum_{i=1}^n \mathbf{1}_{\{|_i Z_t - \pi| < \sigma\}} \delta \left(\frac{d_i Z_t}{dt} \right) \quad (18)$$

with ρ the reaction radius, σ the surface half thickness, π the central height of the surface and the rest is the same as in the previous model. By letting σ and π depend on the (x, y) position, we can thus make a more general surface.

The surface will not be physical correct, because the topological structure can be mimicked to some extent, but the particles only feel the potential surface. The potential surface can be entirely different then the topological form of the real surface, but they are weakly related. For instance if a real surface repeats itself with a certain frequency, then with the same frequency the potential surface will be repeated. The potential surface interacts with the particle in the energy domain. The energy needed to hop or to get free from the surface will vary according to the potential surface. Therefore the reaction and diffusion of a particle are greatly influenced by the position of the particle.

5.3 Model of random walk of voluminous particle

We have assumed that the random walk was Brownian motion. Brownian motion is mathematically described as a Wiener process. In section A.1 you can find more details on Wiener processes.

In this model we use the derivative $\frac{d_i Z_t}{dt}$ of a Wiener process. According to theorem A.1.3 in A.1 are these type of processes almost nowhere differentiable in time. Thus the derivative does not have any mathematical meaning. The derivative does show what the differential equations would be if the Wiener process was replaced by a non-stochastic process. The derivative then shows when a particle stays on the surface.

According to the Ito theorem, theorem A.2.9 in A.2, the stochastic process should not only be differentiated with respect to t but also to W_t , the Wiener process. Therefore we can get a mathematically correct model if we find a way to get an alternative expression for $\frac{d_i Z_t}{dt}$.

The terms $\frac{d_i Z_t}{dt}$ are mathematically easy to derive with the Ito theorem. However without knowledge of stochastic differential equations it can be meant like written in section A.2., like a term independent of random variables and a term dependent on a Gaussian random variable. If we then apply the Ito Doblin theorem on the F_H and W_H terms and then separate the random variable part with the part not dependent on a random variable, then it is possible to get a large

amount of noise terms. If we succeed to catch the $\mathbf{1}_{\{\|\bar{X}_t - \bar{X}_t\| < \rho\}}$ term into a single constant, then it is possible to get a single Wiener process depending on the components of Z_t . Just like lemma A.1.2. shows.

To be able to show that the multiple Wiener processes can be recreated with a single Wiener process it is easier to change the model into a computer program. For computational easy we use a pre-set volume. At every direction we let a particle at the edge reappear at the other end of the direction. For the grain this is reasonable to apply, because a dust grain has normally a surface topological equivalent to the sphere and therefore a kind of two-dimensional repetition. The repetition we use is that of a dust grain with a surface topological equivalent to a torus.

The problem with a grain is that a particle can't penetrate the grain. Brownian motion does not have such a restriction. Therefore a possible solution is to make the grain a double sided surface. Thus that a particle from below the grain going to the grain and a particle above the grain going to the grain, both with the same (x,y) position are actually two particles with the same (x,y) position that do not interact until they are at the surface in each others reaction volume. In this way Brownian motion can be used. The use of Brownian motion in this model does not change the motion properties of the actual particle that it models, because the motion of the particle will still be Brownian motion if you only look at it's path.

The main problem of all deterministic models is the creation and annihilation of particles. Addition of extra molecules or reaction of molecules or diffusion of molecules cause a time dependent amount of particles in the pre-set volume. The use of the repetition condition on the edges resolves the problem for the particles in the gas phase. For the reacting particles it is impossible to apply such a repetition argument to keep the number of particles in the volume constant.

A solution is to let the reacting particles exist as separate and at the moment of reaction just count the reaction. The problem with this solution is the underlying Wiener process. When you numerically model the positions, you will get a certain array of values of N_H, N_{H_2} . Because of the properties of a Wiener process you can zoom in at the time that a particle reacts with another particle. Because of the last assumption, their positions are the same as of the new particles. The distribution of the position increments are Gaussian distributed with variance Δt . Thus when you zoom in far enough, you have a chance of almost always 1 that the two new particles will react again and thus increasing the variable, while it was constant at first. Thus this assumption is very dangerous. The advantages are that the number of particles always stay constant and thus that the computational demands do not change during the process. If you choose the numeric time step large enough, then this problem will not arise, but then the reaction will almost never happen. Thus we need to carefully choose a time step or we need to change the z-direction Brownian motion with a random variable at the moment a reaction occurs. This can be done more easily in a numerical description than in differential equations, because then we need annihilator and creator operators and then we go to the difficult realm of Doi-Peliti. A repair for this problem is to give the two reacting particles a new random position in the volume. Numerically this is easy to implement. For differential equations you still need Doi-Peliti.

Implemented with the solution of all the above problems we get the final model

$$\begin{aligned}
& t_k N_{\text{H}} - t_{k-1} N_{\text{H}} = F_{\text{H}}(t_k - t_{k-1}) + w_{\text{H}}(t_k - t_{k-1}) \times \\
& \times \sum_{i=1}^n \left[\mathbf{1}_{\{|Z_{t_k} - \pi(i\bar{X}_{t_k})| < \sigma(i\bar{X}_{t_k})\}} \mathbf{1}_{\{|Z_{t_{k-1}} - \pi(i\bar{X}_{t_{k-1}})| \geq \sigma(i\bar{X}_{t_{k-1}})\}} \right. \\
& \left. - \mathbf{1}_{\{|Z_{t_k} - \pi(i\bar{X}_{t_k})| \geq \sigma(i\bar{X}_{t_k})\}} \mathbf{1}_{\{|Z_{t_{k-1}} - \pi(i\bar{X}_{t_{k-1}})| < \sigma(i\bar{X}_{t_{k-1}})\}} \right] \\
& - 2a_{\text{H}}(t_k - t_{k-1}) \times \\
& \times \sum_{i=1}^n \sum_{j < i} \left[\mathbf{1}_{\{|Z_{t_k} - \pi(i\bar{X}_{t_k})| < \sigma(i\bar{X}_{t_k})\}} \mathbf{1}_{\{|Z_{t_k} - \pi(j\bar{X}_{t_k})| < \sigma(j\bar{X}_{t_k})\}} \right. \\
& \times \mathbf{1}_{\{|Z_{t_{k-1}} - \pi(i\bar{X}_{t_{k-1}})| < \sigma(i\bar{X}_{t_{k-1}})\}} \\
& \left. \times \mathbf{1}_{\{|Z_{t_{k-1}} - \pi(j\bar{X}_{t_{k-1}})| < \sigma(j\bar{X}_{t_{k-1}})\}} \mathbf{1}_{\{||j\bar{X}_{t_k} - i\bar{X}_{t_k}|| < \rho\}} \right] \quad (19)
\end{aligned}$$

$$\begin{aligned}
& t_k N_{\text{H}_2} - t_{k-1} N_{\text{H}_2} = F_{\text{H}_2}(t_k - t_{k-1}) - W_{\text{H}_2} N_{\text{H}_2} + a_{\text{H}}(t_k - t_{k-1}) \times \\
& \times \sum_{i=1}^n \sum_{j < i} \left[\mathbf{1}_{\{|Z_{t_k} - \pi(i\bar{X}_{t_k})| < \sigma(i\bar{X}_{t_k})\}} \mathbf{1}_{\{|Z_{t_k} - \pi(j\bar{X}_{t_k})| < \sigma(j\bar{X}_{t_k})\}} \right. \\
& \times \mathbf{1}_{\{||j\bar{X}_{t_k} - i\bar{X}_{t_k}|| < \rho\}} \mathbf{1}_{\{|Z_{t_{k-1}} - \pi(i\bar{X}_{t_{k-1}})| < \sigma(i\bar{X}_{t_{k-1}})\}} \\
& \left. \times \mathbf{1}_{\{|Z_{t_{k-1}} - \pi(j\bar{X}_{t_{k-1}})| < \sigma(j\bar{X}_{t_{k-1}})\}} \right] \quad (20)
\end{aligned}$$

$$\begin{aligned}
& i\bar{X}_{t_k} - i\bar{X}_{t_{k-1}} = \sigma \cdot (\mathcal{N}_X(0, t_k - t_{k-1}), \mathcal{N}_Y(0, t_k - t_{k-1}), \mathcal{N}_Z(0, t_k - t_{k-1})) \\
& + (U(0, 2X_{\text{border}}), U(0, 2Y_{\text{border}}), U(0, 2Z_{\text{border}})) \times \\
& \times \sum_{j \neq i} \left[\mathbf{1}_{\{|Z_{t_{k-1}} - \pi(i\bar{X}_{t_{k-1}})| < \sigma(i\bar{X}_{t_{k-1}})\}} \mathbf{1}_{\{|Z_{t_{k-1}} - \pi(j\bar{X}_{t_{k-1}})| < \sigma(j\bar{X}_{t_{k-1}})\}} \right. \\
& \times \mathbf{1}_{\{||j\bar{X}_{t_{k-1}} - i\bar{X}_{t_{k-1}}|| < \rho\}} \mathbf{1}_{\{|Z_{t_{k-2}} - \pi(i\bar{X}_{t_{k-2}})| < \sigma(i\bar{X}_{t_{k-2}})\}} \times \\
& \left. \times \mathbf{1}_{\{|Z_{t_{k-2}} - \pi(j\bar{X}_{t_{k-2}})| < \sigma(j\bar{X}_{t_{k-2}})\}} \right] \text{mod}(2X_{\text{border}}, 2Y_{\text{border}}, 2Z_{\text{border}}) \quad (21)
\end{aligned}$$

with t_k are a sequence of increasing times in a interval $[0, T]$, X_{border} is the position in the X direction of the border of the space that is being modelled, $\mathcal{N}_X(m, s)$ is a normal distributed variable in the X direction with mean m and variance s , σ is the speed of the particles and $U(a, b)$ is a uniform distributed variable with values in the interval (a, b) .

The above model is an Euler approximation of the integral needed to get the solution. The model can be made to use Runge-Kutta 4, but this would be almost impossible to write down in a complete, clear way. For this model we have constructed a program to calculate the formation of H_2 and N_{H} with respect to time. The code can be found in appendix B.

In the code we have made a slight correction. The sum of the reaction term does not know that it can physically only take the values 0 and 1, while in system (16)-(18) it can take the values of 0 till $\frac{1}{2}n(n-1)$ if there are n particles. Therefore in the code a correction is made such that in system (16)-(18) the sum of a_{H} will be replaced by a indicator with the condition that the original sum of a_{H} must be non-zero. This has been done on every place where the sum of a_{H} was needed.

In the continuous case this is not necessary because there will always be one particle the first to reach the reaction zone.

Another correction in this part is the addition of a floor function. This was needed to be able to get rid of certain unwanted conditions, like three H-molecules close together, thus only able to make one H_2 molecule, but without the floor function they make 1.5 H_2 molecules. The floor function can only repair one of such an event. Thus in the low molecule amount limit the floor function is enough. In the high molecule amount limit the floor function is insufficient, but this error is too small to be significant.

As stated before, we use in our numerical model an extra random variable to relocate the reacting H-molecules in order to have only one reaction and new particles to let the total number of H-molecules be back at the original level. This levelling will not be done at the time of the reaction. It will be done one step later. This is done because the reaction always takes time. When the time step becomes smaller, the levelling will happen faster. Thus in the continuous limit the levelling will be immediately. This levelling is not entirely physically justified. The levelling is a crude way of applying the law of large numbers and thus only justified in large amount of molecules. Besides that the levelling is only done on the amount of one species, while it should be on the entire amount of molecules. This is not easy, because arrays should then be dynamical and every particle of H_2 had to be modelled with a Wiener process until it was out of the specified volume. From figure 3 it seems obvious to replace the model

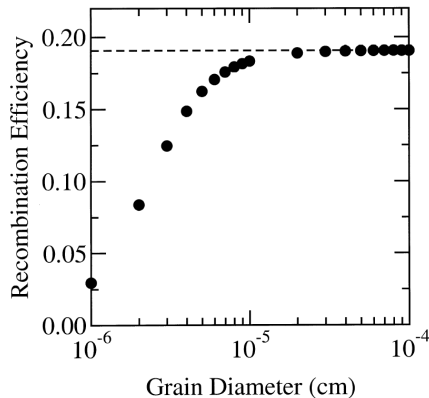


Figure 3: Plot of number of H and H_2 particles and change in H_2 particles against time in rounds. The dotted line is the number of H particles, the striped line is the number of H_2 particles and the solid line are the increments per round for H_2 . The values are 100 particles in a 40 by 40 by 40 box with $F_H = 0, W_H = 1, A_H = 1, F_{H_2} = 0, W_{H_2} = 0, F_{H_2} = 0$. The time step dt equals 1 and the surface is constant with thickness of 18. The reaction distance is 1 and the speed of the particle is 2 position steps per time step.

with all the random walks with a model with a Wiener process on the number of particles. However this can only be an illusion of human interpretation of statistical phenomenon.

6 Second Model

In the stochastic region it is very easy to give a differential equation that governs the reaction process. In the deterministic region it is a bit harder to get the correct differential equation if you assume a decoupling assumption. In the intermediate region it is much harder to define the type of model that has the properties to derive without too much difficulty the governing dynamics.

The use of differential equations in the stochastic region as in the deterministic region implies it to be the correct type of model. It makes the model easier, because the boundary conditions are known with differential equations.

In the deterministic region probability density functions are used, while in the stochastic region stochastic variables are used. Therefore it seems natural to use a technique that is between both. This is possible when the expectation of the stochastic variable still complies to the rate equations and simultaneously the stochastic variable itself complies to a pre-determinate probability density function.

According to the central limit theorem will the number of particles, a sum of position indicators, have a probability density function equal to the normal density function. Therefore in the differential equations it is necessary to have a term that mimics the change in value of the stochastic variable due to its Gaussian probability density function.

A differential equation can normally not cope with a stochastic variable. For a Gaussian distributed stochastic variable we must use Stochastic Differential Equations¹. The Gaussian distributed stochastic variable is split in two parts: the mean and a zero mean Gaussian distributed stochastic variable, in physical words the mean and Brownian motion, in mathematical words the mean and a Wiener process².

We start with the rate equations with the second modification as outlined in section 3.2 as the basis of the new model. We extent the equations of the model with a function times a Gaussian stochastic variable.

According to Stochastic Differential Equations this can only be written as integral equations of the specified rate equations with the extension of Ito-integrals³ of a function.

The Ito-integral has the property that the expectation of the Ito-integral equals zero. When we assume that our model has a so called strong solution⁴ we can use Fubini's theorem, which states that the sequence of evaluating two integrals does not change the outcome of the integrals. Thus assuming a strong solution allows us to interchange an integral and expectation operator as long as the final solution is a strong solution.

¹For the definition and solutions of Stochastic Differential Equations see section A.3.

²For the definition and properties of a Wiener process see section A.1.

³For the definition and properties of Ito-integrals see section A.2.

⁴see section A.3. definition A.3.7. and onwards for definition and properties of strong solutions.

6.1 The second model for the reaction $\text{H} + \text{H} \rightarrow \text{H}_2$.

The formation of molecular hydrogen has been modelled in the deterministic regime with the rate equations. The use of these equations is a good foundation for the intermediate regime. With appropriate modifications a new model will then suffice the boundary condition that the expectation of the number of particles is governed by the rate equations. It was already mentioned that assuming the existence of a strong solution of our model, we can switch integrals and expectations and together with the property that the expectation of an Ito-integral is zero, it is sufficient to extend the rate equations with a noise term. With the usual convention of writing stochastic integral equations in differential equation form we now get for the formation of molecular hydrogen a 2-dimensional system of differential equations

$$dN_{\text{H}} = [F_{\text{H}} - W_{\text{H}}N_{\text{H}} - 2A_{\text{H}}N_{\text{H}}(N_{\text{H}} - 1)] dt + f(t, N_{\text{H}}) dW_t^1 \quad (22)$$

$$dN_{\text{H}_2} = [F_{\text{H}_2} - W_{\text{H}_2}N_{\text{H}_2} + \mu A_{\text{H}}N_{\text{H}}(N_{\text{H}} - 1)] dt + g(t, N_{\text{H}_2}) dW_t^2 \quad (23)$$

with F_{H_i} , W_{H_i} , A_{H_i} and N_{H_i} as specified in section 4.1, $f(t, x), g(t, x) \in \mathcal{L}_T^2$ and W_t^1, W_t^2 are Wiener processes. Because of the previously mentioned properties of expectation and integral we thus have a set of differential equations that comply to the rate equations under the assumption that a strong solution exists for this differential equation.

The noise term is not specified. The specification of the noise term can not be done a priori. According to the master equation approach the probability density function of N_i is solely dependent on the terms F_i , W_i and A_i . Therefore the variation is dependent on these values, which implies that the noise term is solely dependent on these values. Thus the master equation approach implies that every solution of the differential equations (22) & (23) with noise solely depending on those values cannot be discarded.

The variable N_i can be viewed as a sum of indicators of position over all positions of the grain where a species can attach. The central limit theorem then implies that the noise term of N_i should decrease with increasing number of positions on the grain. Because N_i and the number of positions are connected it is still possible that the noise term can increase with increasing N_i .

For convenience in the following derivations it is assumed that the noise term is linear in N_i with i a species. The system of differential equations is then equal to

$$dN_{\text{H}} = [F_{\text{H}} - W_{\text{H}}N_{\text{H}} - 2A_{\text{H}}N_{\text{H}}(N_{\text{H}} - 1)] dt + [\sigma_{\text{H}}N_{\text{H}} + a] dW_t^1 \quad (24)$$

$$dN_{\text{H}_2} = [F_{\text{H}_2} - W_{\text{H}_2}N_{\text{H}_2} + \mu A_{\text{H}}N_{\text{H}}(N_{\text{H}} - 1)] dt + [\sigma_{\text{H}_2}N_{\text{H}_2} + b] dW_t^2 \quad (25)$$

with σ_i the standard deviation of the i th species.

Differential equation (24) is now in a derived form of the stochastic Verhulst equation, see example A.3.5. This is an equation defined as the following: Suppose λ, σ are constants, X_t is the stochastic process and W_t is the Wiener

process, then the stochastic Verhulst equation is defined as

$$dX_t = (\lambda X_t - X_t^2) dt + \sigma X_t dW_t. \quad (26)$$

The solution is equal to

$$X_t = \frac{X_{t_0} e^{[\lambda - \frac{1}{2}\sigma^2](t-t_0) + \sigma(W_t - W_{t_0})}}{1 + X_{t_0} \int_{t_0}^t e^{[\lambda - \frac{1}{2}\sigma^2](s-t_0) + \sigma(W_s - W_{t_0})} ds}. \quad (27)$$

If we do a dimensional analysis on the solution of the differential equation we get that X must be dimensionless and thus must be a fraction. In this case we have to multiply it with the maximum number of particles on the grain. It is now obvious to conclude that the historical rate equation has as solution the stochastic Verhulst equation with $\sigma = 0$. The appropriate transformation of (24) to the stochastic Verhulst equation can be derived very easily. First we have to make fractions. We do this by dividing the number of particles with N , the maximum number of particles on the grain, and modifying the factors in a similar way. This will give different factors. This conversion give rise to the following factors:

$$\overline{F_{H_i}} = \frac{F_{H_i}}{N} \quad (28)$$

$$\overline{W_{H_i}} = W_{H_i} \quad (29)$$

$$\overline{A_{H_i}} = A_{H_i} N \quad (30)$$

$$\overline{N_{H_i}} = \frac{N_{H_i}}{N} \quad (31)$$

We assume the transformation to be a linear transformation. If we also assume that the transformation is of the form $X_t = 2\overline{A_H}(\overline{N_H} - \mu)$ then λ will become the difference between the at most two stationary solutions of the differential equation (24) and μ is a stationary solution of $\overline{N_H}$. The appropriate values must then be the following:

$$-\lambda\mu - 2\overline{A_H}\mu^2 = \overline{F_H} \quad (32)$$

$$\lambda + 4\overline{A_H}\mu = 2\frac{\overline{A_H}}{N} - \overline{W_H} \quad (33)$$

Thus (33) can be rewritten as

$$\lambda = 2\frac{\overline{A_H}}{N} - \overline{W_H} - 4\overline{A_H}\mu \quad (34)$$

The combination of (32) and (34) now yield

$$\left(\overline{W_H} - 2\frac{\overline{A_H}}{N}\right)\mu + 2\overline{A_H}\mu^2 = \overline{F_H} \quad (35)$$

Using the solution of (35) in combination with (34) we get

$$\begin{aligned}\mu_{\pm} &= \frac{1}{2N} - \frac{\overline{W_H}}{4A_H} \pm \sqrt{\left(\frac{1}{2N} - \frac{\overline{W_H}}{4A_H}\right)^2 + \frac{\overline{F_H}}{2A_H}} \\ &= \frac{1}{2N} - \frac{W_H}{4A_H N} \pm \sqrt{\left(\frac{1}{2N} - \frac{W_H}{4A_H N}\right)^2 + \frac{F_H}{2A_H N^2}}\end{aligned}\quad (36)$$

$$\begin{aligned}\lambda_{\pm} &= \mp \sqrt{\left(2\frac{\overline{A_H}}{N} - \overline{W_H}\right)^2 + 8\overline{F_H}A_H} \\ &= \mp \sqrt{(2A_H - W_H)^2 + 8F_H A_H}\end{aligned}\quad (37)$$

The differential equation thus becomes

$$\begin{aligned}d\overline{N_H} &= \left[\overline{F_H} - (\overline{W_H} - 2\overline{A_H}\frac{1}{N})\overline{N_H} - 2\overline{A_H}N_H^2\right] dt \\ &+ \left[\overline{N_H} - \left(\frac{1}{2N} - \frac{\overline{W_H}}{4A_H}\right) \mp \sqrt{\left(\frac{1}{2N} - \frac{\overline{W_H}}{4A_H}\right)^2 + \frac{\overline{F_H}}{2A_H}}\right] \sigma_H \cdot dW_t^1 \\ &= \left[\frac{\overline{F_H}}{N} - \overline{W_H}\overline{N_H} - 2A_H N \overline{N_H} \left(\overline{N_H} - \frac{1}{N}\right)\right] dt \\ &+ \left[\overline{N_H} - \left(\frac{1}{2N} - \frac{W_H}{4A_H N}\right) \mp \frac{1}{N} \sqrt{\left(\frac{1}{2} - \frac{W_H}{4A_H}\right)^2 + \frac{F_H}{2A_H}}\right] \sigma_H \cdot dW_t^1\end{aligned}\quad (38)$$

and the other one becomes

$$\begin{aligned}d\overline{N_{H_2}} &= \left[\overline{F_{H_2}} - \overline{W_{H_2}}\overline{N_{H_2}} + \mu\overline{A_H}N_H \left(\overline{N_H} - \frac{1}{N}\right)\right] dt + \sigma_{H_2}\overline{N_{H_2}}dW_t^2 \\ &= \left[\frac{\overline{F_{H_2}}}{N} - \overline{W_{H_2}}\overline{N_{H_2}} + \mu A_H N \overline{N_H} \left(\overline{N_H} - \frac{1}{N}\right)\right] dt + \sigma_{H_2}\overline{N_{H_2}}dW_t^2\end{aligned}\quad (39)$$

When the noise terms are equal to zero we have a system of differential equations with two stationary solutions. The first is

$$(\overline{N_H}, \overline{N_{H_2}}) = \left(\mu_{\pm}, \frac{\frac{F_{H_2}}{N} + \mu A_H N \mu_{\pm} \left(\mu_{\pm} - \frac{1}{N}\right)}{W_{H_2}}\right).\quad (40)$$

The second is

$$(\overline{N_H}, \overline{N_{H_2}}) = \left(\mu_{\pm} + \frac{\lambda_{\pm}}{2A_H N}, \frac{\frac{F_{H_2}}{N} + \mu A_H N \left(\mu_{\pm} + \frac{\lambda_{\pm}}{2A_H N}\right) \left(\mu_{\pm} + \frac{\lambda_{\pm}}{2A_H N} - \frac{1}{N}\right)}{W_{H_2}}\right).\quad (41)$$

These stationary solutions can only exist if every component is non-negative. Thus μ_- is impossible, when F_H is not equal to zero. Therefore only the stationary solutions with μ_+ and thus λ_+ are the correct physical stationary solutions of the differential equations.

Differential equation (38) differs from (24) in the noise part. (38) has a correction on N_H . This correction causes the noise to be dependent on the difference between the fraction of particles and the first stationary solution. This difference can not be re-corrected easily, because every modification to N_H to get the

correct noise term will make the time term uncorrect. However, the constant in this noise term descends from the constant of the noise term of the fraction differential equation. In that noise term the constant is inverse dependent on N . Therefore this constant will become with large N negligible with respect to the other parts of the noise term. We can now easily give the solution for $\overline{N_{H_i}}$. However if we multiply this answer with N we get the solution for N_i . Thus we get the following solution for N_H :

$$\begin{aligned}
C \cdot N_H(t) &= C \left[\frac{1}{2} - \frac{W_H}{4A_H} \pm \sqrt{\left(\frac{1}{2} - \frac{W_H}{4A_H}\right)^2 + \frac{F_H}{2A_H}} \right] \\
&+ \left(N_H(0) + \frac{W_H}{4A_H} - \frac{1}{2} \mp \sqrt{\left(\frac{1}{2} - \frac{W_H}{4A_H}\right)^2 + \frac{F_H}{2A_H}} \right) \times \\
&\times e^{\left(\mp\sqrt{(W_H-2A_H)^2+8A_H F_H} - \frac{1}{2}\sigma_H^2\right)t + \sigma_H W_t^1} \\
C &= 1 + \frac{1}{N} \left(N_H(0) + \frac{W_H}{4A_H} - \frac{1}{2} \mp \sqrt{\left(\frac{1}{2} - \frac{W_H}{4A_H}\right)^2 + \frac{F_H}{2A_H}} \right) \times \\
&\times \int_{t_0}^t e^{\left(\mp\sqrt{(W_H-2A_H)^2+8A_H F_H} - \frac{1}{2}c^2\right)s + cW_s^1} ds \\
N_H(t) &= \mu_{\pm} + \frac{(N_H(0) - N\mu_{\pm}) e^{(\lambda_{\pm} - \frac{1}{2}\sigma_H^2)t + \sigma_H W_t^1}}{1 + \frac{1}{N} (N_H(0) - N\mu_{\pm}) \int_{t_0}^t e^{(\lambda_{\pm} - \frac{1}{2}\sigma_H^2)s + \sigma_H W_s^1} ds} \quad (42)
\end{aligned}$$

This solution could have been guessed directly from the solution of (24) for N_H . The constants μ_{\pm} en λ_{\pm} are all coefficients of the linear terms and thus would not be affected by the transformation to fraction and viceversa. The solution simplifies the differential equation for N_{H_2} , because the difficulty of the $N_H(N_H - 1)$ term is now replaced by the simplicity of a known function only depending on t . The differential equation (25) is therefore only dependent on t and N_{H_2} . Thus using (102) we get the following solution for N_{H_2} .

$$\begin{aligned}
N_{H_2}(t) &= e^{\sigma_{H_2}[W_t - W_{t_0}] - [W_{H_2} + \frac{1}{2}\sigma_{H_2}^2](t-t_0)} [N_{H_2}(t_0) + \\
&+ \int_{t_0}^t e^{[W_{H_2} + \frac{1}{2}\sigma_{H_2}^2](r-t_0) - \sigma_{H_2}[W_r - W_{t_0}]} \times \\
&\times [\mu A_H N_H(r) (N_H(r) - 1) + F_{H_2}] dr] \quad (43)
\end{aligned}$$

According to the definition A.3.7. of strong solution it is clear that (42) & (43) are strong solutions of the stochastic differential equations (24) & (25). Thus according to A.3.10. the system of equations (42) & (43) are the pathwise unique strong solutions of the system of stochastic differential equations (24) & (25) with the boundary condition that the expectation of (42) & (43) are governed by the rate equations (3) & (4).

6.2 Application of this model to arbitrary surface reactions

It is relatively easy to get the result for a single surface reaction. But for multiple surface reactions it is not easy. This has several reasons. The first reason is the reactions itself. Do you allow three particle interactions? The second reason is the complexity of the reaction scheme. The single surface reaction is easy to solve because it is either linear or it is already in a form with a linear term and a diagonal quadratic form. With the multiple surface reactions it is not a priori known that the reactions are linear or a linear term with a diagonal form. Therefore it is necessary to set restrictions. The first restriction is the restriction on the type of reactions. We only allow the following reaction



such that in the differential equations it give rise to the term: $R_C N_A N_B$, with R_C a reaction specific constant. The second restriction is on the reacting particles. A can be any type of particle, while B can only be an element. This second restrictions simplifies later calculations and derivations.

Let us introduce new notations. The complicated scheme of surface reactions will be called the reaction network. This network can be visualized by a general graph with vertices V and edges E . The first restriction for a single reaction can be visualised as an edge between three vertices, one reaction product vertex and two reaction particle vertices or one reaction particle vertex depending on the equality $A = B$. This type of graph is called hypergraph.⁵ An edge that connects three vertices is called a triple. An edge that connects two vertices is called a normal edge. The degree of an edge is equal to the number of vertices connected to the edge. An n -uniform hypergraph is a graph with only edges of degree n , called n -tuples. Thus a 2-uniform hypergraph is the common graph. A hypergraph can be made a directed hypergraph by replacing the n -tuples with n -arrows. The n -arrow A can then be described as an ordered pair of non-empty sets G and R , where G contains the outgoing (giving) vertices and R contains the ingoing (receiving) vertices such that $|G| + |R| = n$, the degree of the arrow, hold. If the direction of the reaction in (44) is applied to the edge of the reaction, then we get the arrow of the reaction in the directed hypergraph that represents the reaction network. Every arrow points to a more complex molecule. The complexity of a molecule can be indicated with a complexity number that indicates how much atoms are needed to construct one molecule. Thus for example water (H_2O) has complexity number 3. The second restriction implies that if all possible combinations of atoms were allowed, the maximal number of different routes to construct a molecule is equal to the product of the indices of the molecule specification (water has indices 2 and 1 and thus maximal 2 different routes). Chemically there are stability restrictions on the maximum number atoms of an element in one molecule. For instance a molecule consisting of only hydrogen atoms can maximally have 2 atoms in the molecule, while carbon can have any number of atoms in a molecule. Besides the chemical restriction on molecules with only atoms of one species there are restrictions on combinations. Carbon atoms can at most have 4 atoms to bind with. Therefore

⁵For more on Hypergraphs see the book Hypergraphs of C. Berge

if we discard ionic bindings and hydrogen bonds a molecule can be represented by a graph with vertices that represent the atoms and the edges that represent the electron pairs. The total number of formation routes are now given as the total number ways to decompose the graph by removing a vertex and the halves of the associated edges and recombining the surplus components into one component with keeping account of the properties of the atoms. This is one option, another option does not allow the recombining of the surplus components. This can result in different molecules with the same molecular formula that are different vertices in the network. but in the following part of the paper this option will not be used as the foundation of the model. Thus C_2H_6 has only 5 different routes, while one would expect 12 different routes. The total different routes are thus the sum of the amount of different routes to form the molecules with the highest complexity number in their branch. The 5 different routes of C_2H_6 are a result of the 1 valence electron of hydrogen, the 4 valence electrons of carbon and the choice between starting with hydrogen or carbon, resulting in $4+1 = 5$ different routes.

If we discard loops and multiple copies of edges, then the directed hypergraph can be represented with the incidence matrix I . This incidence matrix has dimensions $|V| \times |E|$ if V and E are the sets of vertices and edges respectively. The rank of this matrix is equal to the edgerank of the matrix (edge rank is in this case equal to the column rank of the matrix)

Let N_i be the number of particles of species i , N the maximum number of particles on the grain and X the vector of which the components are the N_i . Then the differential equation of X can be given as

$$dX = [F - WX + DX + A(t, X)] dt + \sigma(X) dW_t \quad (45)$$

with F a vector, W a diagonal desorption matrix, D a diffusion matrix and $A(t, X)$ a surface reaction vector. The surface reaction vector $A(t, X)$ can be given in terms of components of the incidence matrix:

$$\begin{aligned} A^i(t, X) &= \sum_{e \in E} A^e I^{ie} \left(\max_{f \in E} (|G_f| + |R_f|) - |G_e| \right) \\ &\times \prod_{v \in R_e} X_v^{\left[\max_{f \in E} (|G_f| + |R_f|) - |G_e| \right]} \end{aligned} \quad (46)$$

with

$$|G_e| = \sum_{k \in V} \frac{1}{2} \left[(I^{ke})^2 + I^{ke} \right], \quad (47)$$

$$|R_e| = \sum_{k \in V} \frac{1}{2} \left[(I^{ke})^2 - I^{ke} \right], \quad (48)$$

A^e the reaction constant belonging to the reaction of edge e , V the vertices of the reaction network, E the set of arrows $e = (G_e, R_e)$ in the reaction network, X_v the component of X corresponding to vertex v and $I^{ke} \in \{-1, 0, 1\}$ is the component of the incidence matrix I with vertex k and edge e .

In the case of the formation of H_2 the differential equation (45) will take the following form.

$$dN_H = [F_H - (W_H - A)N_H + \mu_D DN_{H_2} - AN_H^2] dt + \vec{U}(N_H, N_{H_2}) \cdot d\vec{W}_t \quad (49)$$

$$dN_{H_2} = [F_{H_2} - (W_H + D)N_{H_2} - \mu_A AN_H + \mu_A AN_H^2] dt + \vec{V}(N_H, N_{H_2}) \cdot d\vec{W}_t \quad (50)$$

with μ_D, μ_A coefficients of the specific processes and U and V vector noise functions equal to the standard deviation.

Just like with equation (22) the differential equation can be transformed into a form closely related to the stochastic Verhulst equation. However this transformation does not bring us closer to the solution, except when D is equal to 0 because then (49) and (50) are equal to (22) and (23).

For the case where D is not equal to zero it is possible due to the existence of noise terms to completely solve the differential equation.

Assume that N_{H_2} is equal to $\frac{1}{\mu_D D} (AN_H(N_H - 1) + bN_H + c)$ with b, c parameters. Then the differential equations (49) and (50) will be equal to differential equations (51) and (52) respectively.

$$dN_H = [F_H + c + (b - W_H)N_H] dt + \vec{U}(N_H) \cdot d\vec{W}_t \quad (51)$$

$$dN_{H_2} = [F_{H_2} - \mu_A \mu_D Dc + (\mu_A \mu_D D - W_{H_2} - D)N_{H_2} + \mu_A \mu_D D b N_H] dt + \vec{V}(N_H, N_{H_2}) \cdot d\vec{W}_t \quad (52)$$

According to the Ito theorem (52) must be equal to the stochastic differential equation caused by the assumed form of N_{H_2} . Thus (52) must be equal to (53).

$$\begin{aligned} dN_{H_2} &= d \left[\frac{1}{\mu_D D} (AN_H(N_H - 1) + bN_H + c) \right] \\ &= \frac{1}{\mu_D D} \left[(A(2N_H - 1) + b)(F_H + c + (b - W_H)N_H) + |\vec{U}|^2 A \right] dt \\ &\quad + \left[(A(2N_H - 1) + b)\vec{U}(N_H) \cdot d\vec{W}_t \right] \end{aligned} \quad (53)$$

If we assume that all components of \vec{U} are linear, then component i of \vec{U} is equal to $f_i N_H + g_i$, with f_i, g_i for all i are parameters. This allows (53) to be equal to (54).

$$\begin{aligned} dN_{H_2} &= \sum_i \left[\frac{b - A}{\mu_D D} g_i + \left(\frac{A + b}{\mu_D D} f_i + \frac{2A}{\mu_D D} g_i \right) N_H + \right. \\ &\quad \left. + \frac{2A}{\mu_D D} f_i N_H (N_H - 1) \right] dW_t^i \\ &\quad + \left[\left((F_H + c)(b - A) \frac{1}{\mu_D D} + \sum_i \frac{2A}{\mu_D D} g_i^2 \right) \right. \\ &\quad \left. + \left((b + A)(b - W_H) \frac{1}{\mu_D D} + \frac{2A}{\mu_D D} (F_H + c) + \right. \right. \\ &\quad \left. \left. + \frac{2A}{\mu_D D} \sum_i (2f_i g_i + f_i^2) \right) N_H \right] dt \end{aligned}$$

$$\begin{aligned}
& + \left(\frac{2A}{\mu_D D} \left(b - W_H + \sum_i f_i^2 \right) \right) N_H (N_H - 1) \Big] dt \\
= & \left[-\frac{2c}{\mu_D D} \left(b - W_H + \sum_i f_i^2 \right) + \frac{2b}{\mu_D D} \left(b - W_H + \sum_i f_i^2 \right) N_H \right. \\
& + 2 \left(b - W_H + \sum_i f_i^2 \right) N_{H_2} \Big] dt \\
& + \sum_i \left[2f_i N_{H_2} + \frac{1}{\mu_D D} ((A - b) f_i + 2Ag_i) N_H + \right. \\
& \left. + \frac{b - Ag_i - 2f_i c}{\mu_D D} \right] dW_t^i \tag{54}
\end{aligned}$$

To have equality between (53) and (54) the differential equations have to satisfy a set of equations numbered (55) to (58). In addition we assume component i of \vec{V} to be equal to $k_i N_{H_2} + l_i$.

$$(A - 3b) f_i + 2Ag_i = 0 \tag{55}$$

$$\frac{1}{2} \mu_A \mu_D D - \frac{1}{2} W_{H_2} - \frac{1}{2} D = b - W_H + \sum_i f_i^2 \tag{56}$$

$$(F_H + c)(b - A) + \sum_i 2Ag_i^2 = -c(\mu_a \mu_D D - W_H - D) \tag{57}$$

$$\begin{aligned}
& (b + A)(b - W_H) + 2A(F_H + c) + 2A \sum_i (2f_i g_i + f_i^2) = \\
& = -b(\mu_A \mu_D D - W_H - D) \tag{58}
\end{aligned}$$

These equations are such that the parameters b, c, f_i, g_i are sufficient to solve these equations. Simultaneously k_i is equal to $2f_i$ and l_i is equal to $\frac{b - Ag_i - 2cf_i}{\mu_D D}$. Note that equation (55) is not necessary because N_H is a known function of t and thus will the term of N_H be found in the function l_i .

Equation (51) can now be solved with equation (117) and f_i, g_i as defined with equations (55) to (58) and equation (52) is solved with the assumed dependency of N_H on N_{H_2} with b, c as defined with equations (55) to (58).

The solution of the formation of H_2 is the same for all the formations of homatomic diatomic molecules such as O_2, N_2 , etc. For the formation of a heteroatomic diatomic molecules, such as the radical OH, it is possible to give a similar system of differential equations.

We use the shorthand notation X, Y and Z for the three species. Z is the species to be formed out of X and Y . The differential equations for X, Y and Z .

$$dX = [F_X - W_X X + \mu_D D Z - AXY] dt + \sigma_X^{\vec{v}}(X, Y, Z) \cdot d\vec{W}_t \tag{59}$$

$$dY = [F_Y - W_Y Y + \mu_D D Z - AXY] dt + \vec{\sigma}_Y(X, Y, Z) \cdot d\vec{W}_t \quad (60)$$

$$dZ = [F_Z - (W_Z + D) Z + \mu_A AXY] dt + \vec{\sigma}_Z(X, Y, Z) \cdot d\vec{W}_t \quad (61)$$

The solution of this differential equation can be received quite easily if the same method is used as with the homo-atomic case. The method is based on linearisation of the differential equations of X and Y , such that the differential equation of Z is linear in Z , X , Y and XY , with X , Y and XY known functions of t due to the linearisation of the differential equations of X and Y . The appropriate solution of Z is (62).

$$Z = \frac{1}{\mu_D D} [AXY + aX + bY + c] \quad (62)$$

with a, b and c parameters. This transformation changes the differential equations (59) to (61) into (63) to (65), with the noise terms of X, Y linear in X and Y .

$$dX = [F_X + c + (a - W_X) X + bY] dt + \sum_i (f_i X + g_i Y + h_i) dW_t^i \quad (63)$$

$$dY = [F_Y + c + (b - W_Y) Y + aX] dt + \sum_i (k_i X + l_i Y + m_i) dW_t^i \quad (64)$$

$$dZ = \left[F_Z - \frac{\mu_{AC}}{\mu_D D} + (\mu_A \mu_D D - W_Z - D) Z - \frac{\mu_{AC}}{\mu_D D} X - \frac{\mu_{AC}}{\mu_D D} Y \right] dt + \sum_i (n_i Z + p_i X + q_i Y + r_i) dW_t^i \quad (65)$$

with $f_i, g_i, h_i, k_i, l_i, m_i, n_i, p_i, q_i, r_i$ parameters. Then (65) must according to the Ito theorem be equal to (66).

$$\begin{aligned} dZ &= \frac{1}{\mu_D D} [AXdY + AYdX + adX + bdY \\ &\quad + A \sum_i (f_i X + g_i Y + h_i) (k_i X + l_i Y + m_i) dt] \\ &= \left[\frac{A}{\mu_D D} (a + b - W_X - W_Y) + \frac{Aa}{\mu_D D} X^2 + \frac{Ab}{\mu_D D} Y^2 \right. \\ &\quad + \frac{1}{\mu_D D} (a^2 + ab - aW_X + AF_Y + Ac) X \\ &\quad + \frac{1}{\mu_D D} (b^2 - ab - bW_Y + AF_X + Ac) Y + \frac{aF_X + bF_Y + (a+b)c}{\mu_D D} \\ &\quad \left. + \frac{A}{\mu_D D} \sum_i (f_i X + g_i Y + h_i) (k_i X + l_i Y + m_i) \right] dt \\ &\quad + \frac{A}{\mu_D D} \sum_i [(f_i + l_i) XY + g_i Y^2 + h_i Y + k_i X^2 + m_i X] dW_t^i \\ &= \left[\left(a + b - W_X - W_Y + \sum_i (f_i l_i + g_i k_i) \right) Z \right. \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{\mu_D D} \left(aW_Y + AF_Y + Ac - a \sum_i (f_i l_i + g_i k_i) + A \sum_i (h_i k_i + m_i f_i) \right) X \\
& + \frac{1}{\mu_D D} \left(bW_X + AF_X + Ac - b \sum_i (f_i l_i + g_i k_i) + A \sum_i (h_i k_i + m_i f_i) \right) Y \\
& + \frac{1}{\mu_D D} \left(Aa + \sum_i f_i k_i \right) X^2 + \left(Ab + \sum_i g_i l_i \right) Y^2 \\
& + \frac{1}{\mu_D D} \left(aF_X + bF_Y - (a+b)c + 2c(W_X + W_Y) + A \sum_i h_i m_i \right) dt \\
& + \sum_i \left[\frac{A}{\mu_D D} k_i X^2 + \frac{A}{\mu_D D} g_i Y^2 + (l_i + f_i) Z + \left[\frac{A}{\mu_D D} m_i - a(l_i + f_i) \right] X \right. \\
& \left. + \left[\frac{A}{\mu_D D} h_i - b(l_i + f_i) \right] Y - (l_i + f_i) c \right] dW_t^i \tag{66}
\end{aligned}$$

To make equations (65) and (66) equal to each other we get the set of equations (67) to (70).

$$\begin{aligned}
F_Z - \frac{\mu_{AC}}{\mu_D D} &= \frac{1}{\mu_D D} \left(aF_X + bF_Y - (a+b)c + 2c(W_X + W_Y) + A \sum_i h_i m_i \right) \\
& + \frac{1}{\mu_D D} \left(Aa + \sum_i f_i k_i \right) X^2 + \left(Ab + \sum_i g_i l_i \right) Y^2 \tag{67}
\end{aligned}$$

$$\mu_A \mu_D D - W_Z - D = a + b - W_X - W_Y + \sum_i (f_i l_i + g_i k_i) \tag{68}$$

$$-\mu_{AC} = aW_Y + AF_Y + Ac - a \sum_i (f_i l_i + g_i k_i) + A \sum_i (h_i k_i + m_i f_i) \tag{69}$$

$$A(F_X - F_Y) + bW_X - aW_Y = 0 \tag{70}$$

These equations determine the parameters $a, b, c, f_i, g_i, h_i, k_i, l_i$ and m_i , but a, b and c cannot be time dependent. The solution of equations (63) and (64) can now be given with help of equation (130). Then X and Y are known functions of t . Therefore (117) will give the solution of Z .

Therefore we can summarize these two results as follows:
A reaction $X + Y \rightarrow Z$ with the differential equations

$$dX = [F_X - W_X X + \mu_D DZ - AXY] dt + \sum_i (f_i X + g_i Y + h_i) dW_t^i \tag{71}$$

$$dY = [F_Y - W_Y Y + \mu_D DZ - AXY] dt + \sum_i (k_i X + l_i Y + m_i) dW_t^i \tag{72}$$

$$dZ = [F_Z - (W_Z + D_Z) Z + \mu_A AXY] dt + \sum_i (p_i X + q_i Y + r_i Z + s_i) dW_t^i \tag{73}$$

with $f_i, g_i, h_i, k_i, l_i, m_i, p_i, q_i, r_i$ and s_i not specified, can be solved with the equation $Z = \frac{A}{\mu_D D} XY + aX + bY + c$. Then (71) and (72) are linear and can be solved with (130) and with the solutions for X and Y known, is the solution of Z known as well.

With this result it is in the reaction network quite easy to give the correct solution of the differential equation if the reaction network does receives a 'solution possible' out of the following network of questions:

1. The undirected variant of the network is connected? 'Yes' go to question three, 'No' go for every connected component to question 1.
2. Does there exist an arrow in the network with degree greater than 3? 'Yes', then there is 'no easy solution possible'. 'No', go to question 3.
3. Does for every species, that is not an element, the minimal subnetwork of the reaction network, that is needed to formate the species out of elements, consists of a single path of edges? 'Yes', then there is a 'solution possible'. 'No', go to question 4.
4. When the method of solution given below this set of questions is applied for all the species with multiple paths of formation to the subnetwork of the species with multiple paths of formation. Do for all species with multiple paths of formation all the different paths give exactly the same dependency on the solution of the elements? 'Yes', then there is a 'solution possible'. 'No', then there is 'no easy solution possible'

For the reaction networks with 'solution possible' the way of solving is by applying to all the reactions in the reaction network the way of solving a system of differential equations of one reaction. Then the elements have a linear differential equation, that can be solved with (102), and all the other species have a uniquely defined relationship with the solution of the elements.

The given solution for the 2-in-1-out reaction $X + Y \rightarrow Z$ can be extended to the m -in-1-out reaction $X_1 + X_2 + \dots + X_m \rightarrow Z$ reaction in which the reaction term is $A \prod_i X_i$. Then the reaction can be solved with the equation $Z = a \prod_i X_i + \sum_i b_i X_i + c$. The m reacting species are now allowed to be also non-elements, however the only demand for the product species is that it dissociates back into the m reacting particles.

For the n -in- m -out reaction there exists a problem. The differential equations of the n reacting species does not need to have any more the dissociation term of the product species. Thus totally different species than the reacting species can be the species into which the product species decays. This influences the differential equations to the extent that the previous method is not valid any more. Further research should be required for a solution of these type of problems.

7 Discussion

The use of stochastic differential equations is controversial. The arguments used are that the densities are at rates that the probability density can be assumed to be Gaussian instead of a more complex density function. Secondly the use of stochastic differential equations is an explicit calculation of the normal rate equations with a Gaussian probability density function for the noise. Thus stochastic differential equations do not need to have a larger range of validity than the normal rate equations.

The brief notice of the usage of the SDE's in a network can be oversimplified. With a more elaborate discussion of the topic would allow more insight and probably a more fruitful approach for the problems of the circuits in a general network.

The consistency of the model with the master equation approach is totally absent. The validity of the use of SDE's is made via a model based on the foundations of the master equation approach but eventually only a quantitative argument is used instead of compelling sets of data proving the alleged connection.

8 Conclusion

A mathematical model for the grain-particle surface reaction has been given in the form of Stochastic Differential Equations.

These equations allow a low computational order due to the ability of some equations to have an analytical solution. Furthermore is the computational order low due to a system of only two stochastic differential equations.

With the change of different densities of H-gas will the solutions still remain stable if a strong solution can be found. If there is no strong solution, then the stability can not be guaranteed.

The stochastic differential equations are based on the rate equations. The properties of the stochastic differential equations imply that the continuous rate equations will be retained in the limit of large numbers. This will also cause consistency in the stochastic region. However in the deterministic region it is not known whether these equations are consistent with the master equations. The consistency region has been extended due to a correction in the number of possible collisions.

The model has the properties that for a tree the differential equations can be solved sequentially. For a little more advanced network there still exist solutions, however for a circuit in the network difficulties arise. Although the use of fractions seems to solve a few problems. More research is necessary to solve these difficulties for arbitrary networks.

Thus concluding three of the four goals have been reached with significant comments on the validity of the results.

A Stochastic Differential Equations

⁶ In every day life processes are macroscopic and are very well described by laws of physics. Most of the times differential equations are used to model complex processes. Experiments have the problem that there is always noise that can't be filtered. This noise often originates from the particle nature of objects. Thus the noise possesses information about the particles. Einstein showed in one of his papers of 1905 that the motion of a particle in water can be described by a random motion called Brownian motion. Einstein assumed that the underlying physical process were the collisions of very tiny particles with the object. Brownian motion has the property that all the increments are random and Gaussian distributed. Thus a macroscopic differential equation based on the position of the particle has the problem that it isn't defined. Therefore a new type of differential equation had to be created. This type is called Stochastic Differential Equation or SDE. The foundations of this theory were set by the mathematicians Norbert Wiener, Wolfgang Doblin and Kyoshi Ito. Their work is still reflected in the names of the different mathematical subjects, objects and theorems.

A.1 Wiener Process

The heart of SDE are the Wiener processes. These processes are the mathematical objects that govern Brownian motion and are the sources of the Gaussian random noise. It has the following definition:

Definition. *A.1.1. A Wiener process is a set $W = \{W(t), t \geq 0\}$ with independent increments and the following three properties:*

1. $W(0) = 0$ with probability of 1 (w.p.1)
2. $\mathbb{E}(W(t)) = 0$
3. $\text{Var}(W(t) - W(s)) = t - s$ for all $0 \leq s \leq t$.

To have differential equations with a Wiener process term correctly defined we have to investigate the differentiability of a Wiener process.

Lemma. *A.1.2. Let $W(t)$ denote a Wiener process, then $tW(\frac{1}{t})$ and $W(t+s) - W(s)$ for fixed s are Wiener processes.*

Proof. *Remark that the following hold for a standard Wiener process $W(t)$:*

$$\lim_{t \rightarrow \infty} \mathbb{E} \left(\frac{W(t)}{t} \right) = \lim_{t \rightarrow \infty} \frac{\mathbb{E}(W(t))}{t} = \lim_{t \rightarrow \infty} \frac{1}{t} \cdot 0 = 0 \quad (74)$$

$$\lim_{t \rightarrow \infty} \mathbb{E} \left(\frac{W^2(t)}{t^2} \right) = \lim_{t \rightarrow \infty} \frac{\mathbb{E}(W^2(t))}{t^2} = \lim_{t \rightarrow \infty} \frac{t}{t^2} = \lim_{t \rightarrow \infty} \frac{1}{t} = 0 \quad (75)$$

⁶This section has been based on the book about Stochastic Differential Equations by Kloeden & Platen. Therefore it has great similarities to certain sections of that book. This is the intention, because the book is very clear about the topics. All the material written down in this section is of vital importance to understand the properties of the mathematical objects and the derivations in the previous sections.

Thus $\lim_{t \rightarrow \infty} \frac{W(t)}{t} = 0$ with probability of 1.
Let $f(t)$ be $tW\left(\frac{1}{t}\right)$, then the following hold.

$$\begin{aligned} f(t) - f(s) &= tW\left(\frac{1}{t}\right) - sW\left(\frac{1}{s}\right) \\ &= t\left[W\left(\frac{1}{t}\right) - W\left(\frac{1}{s}\right)\right] + (t-s)W\left(\frac{1}{s}\right) \end{aligned} \quad (76)$$

$$f(0) = \lim_{t \downarrow 0} f(t) = \lim_{t \downarrow 0} tW\left(\frac{1}{t}\right) = \lim_{s \rightarrow \infty} \frac{W(s)}{s} = 0 \text{ w.p.1} \quad (77)$$

$$\mathbb{E}(f(t)) = \mathbb{E}\left(tW\left(\frac{1}{t}\right)\right) = t\mathbb{E}\left(W\left(\frac{1}{t}\right)\right) = t \cdot 0 = 0 \quad (78)$$

$$\mathbb{E}(f^2(t)) = \mathbb{E}\left(t^2W^2\left(\frac{1}{t}\right)\right) = t^2\mathbb{E}\left(W^2\left(\frac{1}{t}\right)\right) = t^2 \cdot \frac{1}{t} = t \quad (79)$$

The first line gives the independence of the increments and thus $tW\left(\frac{1}{t}\right)$ is a standard Wiener process. Let $g(t)$ be $W(t+s) - W(s)$ for fixed s , then the following hold.

$$\begin{aligned} g(t+h) - g(t) &= W(t+h+s) - W(s) - W(t+s) + W(s) \\ &= W(t+h+s) - W(t+s) \\ g(0) &= W(0+s) - W(s) = 0 \text{ w.p.1} \end{aligned} \quad (80)$$

$$\begin{aligned} \mathbb{E}(g(t)) &= \mathbb{E}(W(t+s) - W(s)) = \mathbb{E}(W(t+s)) - \mathbb{E}(W(s)) \\ &= 0 - 0 = 0 \end{aligned} \quad (81)$$

$$\begin{aligned} \mathbb{E}(g^2(t)) &= \mathbb{E}\left([W(t+s) - W(s)]^2\right) \\ &= \mathbb{E}(W^2(t+s)) - 2\mathbb{E}([W(t+s) - W(s)]W(s)) - \mathbb{E}(W^2(s)) \\ &= t+s - 0 \cdot 0 - s = t \end{aligned} \quad (82)$$

The first line gives the independence of the increments and therefore the process $W(t+s) - W(s)$ is a standard Wiener process. □

We have now proven that $\{tW\left(\frac{1}{t}\right), t \geq 0\}$ is a Wiener process and thus the following version of the *Law of the Iterated Logarithm* can be applied:

$$\limsup_{t \downarrow 0} \frac{W(t)}{\sqrt{2t \ln \ln \left(\frac{1}{t}\right)}} = 1 \quad , \quad \liminf_{t \downarrow 0} \frac{W(t)}{\sqrt{2t \ln \ln \left(\frac{1}{t}\right)}} = -1 \quad (83)$$

With these laws it is now possible to look at the differentiability of a Wiener process.

Theorem. *A.1.3. Let $W(t)$ be a Wiener process, then $W(t)$ is almost nowhere differentiable.*

Proof. *From the previous lemma we know that $W(t+s) - W(s)$ is a Wiener process for fixed s , thus the Law of the Iterated Logarithm holds. Thus from (16) there exists for any $\epsilon > 0$ sequences $t_n, t'_n \downarrow 0$ such that hold when n is sufficiently large:*

$$\frac{W(t_n + s) - W(s)}{t_n} \geq (1 - \epsilon) \sqrt{\frac{2 \ln \ln \left(\frac{1}{t_n}\right)}{t_n}} \quad (84)$$

$$\frac{W(t'_n + s) - W(s)}{t'_n} \geq (-1 + \epsilon) \sqrt{\frac{2 \ln \ln \left(\frac{1}{t'_n}\right)}{t'_n}} \quad (85)$$

Using the following expression

$$\lim_{t \downarrow 0} \frac{2 \ln \ln \left(\frac{1}{t}\right)}{t} = \lim_{s \rightarrow \infty} 2s \ln \ln(s) = \infty \quad (86)$$

we have the following limits:

$$\lim_{t_n \downarrow 0} \frac{W(t_n + s) - W(s)}{t_n} = \infty \quad , \quad \lim_{t'_n \downarrow 0} \frac{W(t'_n + s) - W(s)}{t'_n} = -\infty \quad (87)$$

Since the limits hold almost surely, $W(t)$ can not be differentiable for $t = s$ for all $s \geq 0$ almost surely. Thus $W(t)$ is almost nowhere differentiable. \square

This proof is not rigorous enough, because the proof depends on the path of the Wiener process. It can be made rigorous, but this would not make it easier to understand. For a rigorous proof go to section 2.4 of Kloeden & Platen.

A.2 Ito integrals and Ito theorem

Like many other mathematical objects differential equations can be seen as a restricted version of another mathematical object. In this case the integral equation. The restriction is set for the differential equation on the set of functions that are solutions. The difference is the following: every function that can be differentiated can be integrated but not otherwise.

This implies an ordinary differential equation cannot have a Wiener process as solution, while an integral equation would not have problems with the differentiability. The problems arise in the definition of the integral. If we use the Riemann, Lebesgue or Riemann-Stieltjes integral, then a Wiener process cannot be a solution because of the infinitely many discontinuities and the unbounded variation of the Gaussian increments.

If we want to have a differential equation with an extra random independently distributed Gaussian increment, ξdt , we thus have a serious problem.

If we only have such a stochastic term in the differential equation, then we are tempted to use a Wiener process as solution. But we can't because formally a Wiener process can't be differentiated. Thus if we rewrite the differential equation into an integral equation and suggestively replace the ξdt with the term dW_t then this integral cannot be a Riemann, Lebesgue or Riemann-Stieltjes integral for the reasons stated above. Thus a totally new type of integral has to be invented.

Suppose we have the differential equation $dX_t = b(t)\xi dt$, then we would expect the solution $b\{W_t - W_{t_0}\}$ when $b(t)$ equals the constant b .

This expected property of the new type of integral is the main idea to be able to construct the new integral. Therefore we have to introduce notations to simplify the construction.

First let f denote a random function over the unit time interval $0 \leq t \leq 1$ and let us denote the integral of f by $I(f)(\omega)$. Then with abuse of notation the following must hold

$$I(f)(\omega) = \int_0^1 f(s, \omega) dW_s(\omega) \quad (88)$$

Obviously this will become our notation of the new type of integral.

The expected property must hold for every function f in \mathcal{L}^2 . To rigorously define this we must be more specific about the space and the functions we use. Thus let $(\Omega, \mathcal{A}, \mathcal{P})$ be a probability space, $W = \{W_t, t \geq 0\}$ a Wiener process and $\{\mathcal{A}_t, t \geq 0\}$ an increasing family of sub- σ -algebras of \mathcal{A} such that W_t is \mathcal{A}_t -measurable and the following hold:

$$E(W_t | \mathcal{A}_0) = 0 \quad E(W_t - W_s | \mathcal{A}_s) = 0 \quad w.p.1 \text{ for all } 0 \leq s \leq t \quad (89)$$

The interpretation of \mathcal{A}_t is of a set of events that can be detected before of at time t . This is necessary, because any event prior to t must not effect the distribution of the Wiener process. This is called nonanticipativeness with respect to the Wiener process.

Let \mathcal{L}_T^2 for $0 < T < \infty$ be a class of functions $f : [0, T] \times \Omega \rightarrow \mathbb{R}$ with the following properties.

1. f is jointly $\mathcal{L} \times \mathcal{A}$ -measurable
2. $\|f(t, \cdot)\|_{2, T}^2 = \int_0^T \mathbb{E} \left(f(t, \cdot)^2 \right) dt < \infty$
3. $\mathbb{E} \left(f(t, \cdot)^2 \right) < \infty$ for each $0 \leq t \leq T$
4. $f(t, \cdot)$ is \mathcal{A}_t -measurable for each $0 \leq t \leq T$

Let $\{t_i^n, i \in \{0, \dots, N\}\} \subset [t_0, T]$ with $t_0 = t_0^n < t_1^n < \dots < t_n^n = T$ be a partition of times in the interval such that $\max_i (t_i^n - t_{i-1}^n) = \Delta_n$ and $\lim_{n \rightarrow \infty} \Delta_n = 0$.

Then we define a step function f , i.e. $f(t, \omega) = f_i$ for $t \in [t_{i-1}^n, t_i^n]$ with $i = 1, 2, \dots, n$. Then the integral of 2 is of the form:

$$\int_0^T \mathbb{E} \left(f(t, \cdot)^2 \right) dt = \sum_{i=1}^n \mathbb{E} (f_i^2) (t_i - t_{i-1}) \quad (90)$$

Because the set of step functions, \mathcal{S}_T^2 , is dense in \mathcal{L}_T^2 ⁷, which is a Banach space if we do not distinguish functions differing only on a set of measure zero, is the integral of 2 defined for \mathcal{L}_T^2 . Remember that the functions already satisfied property 2, but the way the integral had to be interpreted was not clear. Thus we can now define the new integral, which we call Ito integral, on \mathcal{S}_T^2 .

Definition. *A.2.1. Let $f \in \mathcal{S}_T^2$ with a partition $0 < t_0 < t_2 < \dots < t_n = T$ and random variables f_1, f_2, \dots, f_n . Then the Ito integral of f , notation $I(f)(\omega)$, is defined as:*

$$I(f)(\omega) = \sum_{i=1}^n f_i(\omega) [W_{t_i}(\omega) - W_{t_{i-1}}(\omega)] \quad w.p.1 \quad (91)$$

Property 4 implies that f_i is $\mathcal{A}_{t_{i-1}}$ -measurable.

In the previous section it was not mentioned that the Wiener process is a martingale. But now we need a few properties of the martingale Wiener process:

1. $W_{t_i} - W_{t_{i-1}}$ is \mathcal{A}_{t_i} -measurable
2. $\mathbb{E} (W_{t_i} - W_{t_{i-1}} | \mathcal{A}_{t_i}) = 0$
3. $\mathbb{E} \left[(W_{t_i} - W_{t_{i-1}})^2 | \mathcal{A}_{t_i} \right] = t_i - t_{i-1}$

For the sub- σ -algebras we have the following rule: $\mathcal{A}_{t_{i-1}} \subset \mathcal{A}_{t_i}$. Thus the product $f_i (W_{t_i} - W_{t_{i-1}})$ is \mathcal{A}_{t_i} -measurable for $i = 1, 2, \dots, n$. This implies $I(f)$ is \mathcal{A}_T -measurable.

The products are also integrable over Ω and each term is mean-square integrable. Thus the Ito-integral $I(f)$ is integrable. Therefore determining the expectation of the Ito integral is possible.

⁷The proof of this assertion will not be given here. The proof can be found on pages 82-83 of Kloeden & Platen.

Lemma. A.2.2. Let $f, g \in \mathcal{S}_T^2$ be a step function, $W = \{W_t | t \in [0, T]\}$ be a Wiener process and $\alpha, \beta \in \mathbb{R}$, then the following properties of the Ito integral hold:

1. $\mathbb{E}(I(f)) = 0$
2. $\mathbb{E}(I(f)^2) = \int_0^T \mathbb{E}(f(t, \cdot)^2) dt$
3. $I(\alpha f + \beta g) = \alpha I(f) + \beta I(g)$

Proof. Proof of property one. We have shown earlier that $I(f)$ is integrable. Thus the notation $\mathbb{E}(I(f))$ is not meaningless. Together with the definition of Ito-integral for a function $f \in \mathcal{S}_T^2$ we get:

$$\begin{aligned}
\mathbb{E}(I(f)) &= \mathbb{E}\left(\sum_{i=1}^n f_i [W_{t_i} - W_{t_{i-1}}]\right) \\
&= \sum_{i=1}^n \mathbb{E}(f_i [W_{t_i} - W_{t_{i-1}}]) \\
&= \sum_{i=1}^n \mathbb{E}(f_i) \mathbb{E}(W_{t_i} - W_{t_{i-1}} | \mathcal{A}_{t_{i-1}}) \\
&= 0
\end{aligned} \tag{92}$$

Thus property one is proven.

Proof of property two. The square of the integral is a problem, because it is a square of a sum and it is not known if all the functions are measurable. If you look at $f_{i-1} f_j [W_{t_i} - W_{t_{i-1}}]$, then it is only $\mathcal{A}_{t_{j-1}}$ -measurable for $i \leq j$. This allows the following derivation:

$$\begin{aligned}
\mathbb{E}(I(f)^2) &= \mathbb{E}\left(\left[\sum_{i=1}^n f_i [W_{t_i} - W_{t_{i-1}}]\right]^2\right) \\
&= \mathbb{E}\left(\sum_{i=1}^n f_i^2 [W_{t_i} - W_{t_{i-1}}]^2 \right. \\
&\quad \left. + \sum_{i=1}^n \sum_{j=1}^n f_i f_j [W_{t_i} - W_{t_{i-1}}] [W_{t_j} - W_{t_{j-1}}]\right) \\
&= \sum_{i=1}^n \mathbb{E}(f_i^2 [W_{t_i} - W_{t_{i-1}}]^2) \\
&\quad + \sum_{i=1}^n \sum_{j=1}^n \mathbb{E}(f_i f_j [W_{t_i} - W_{t_{i-1}}] [W_{t_j} - W_{t_{j-1}}]) \\
&= \sum_{i=1}^n \mathbb{E}(f_i^2) \mathbb{E}([W_{t_i} - W_{t_{i-1}}]^2 | \mathcal{A}_{t_{i-1}}) \\
&\quad + \sum_{i=1}^n \sum_{j=1}^n \mathbb{E}(f_i f_j [W_{t_i} - W_{t_{i-1}}]) \mathbb{E}([W_{t_j} - W_{t_{j-1}}] | \mathcal{A}_{t_{j-1}})
\end{aligned}$$

$$\begin{aligned}
&= \sum_{i=1}^n \mathbb{E}(f_i^2) \mathbb{E}\left([W_{t_i} - W_{t_{i-1}}]^2 \mid \mathcal{A}_{t_{i-1}}\right) \\
&= \sum_{i=1}^n \mathbb{E}(f_i^2) (t_i - t_{i-1}) \\
&= \int_0^T \mathbb{E}\left(f(t, \cdot)^2\right) dt \tag{93}
\end{aligned}$$

Thus property two is proven.

Proof of property three. When the functions and constants are as given, then $\alpha f + \beta g \in \mathcal{S}_T^2$ holds. The partition of this new function is equal to the union of the partitions of f and g . Thus we can determine the Ito-integral of $\alpha f + \beta g$. The linear property of the integral is due to the linear property of the sum operator and that it sums over a linear combination in \mathcal{S}_T^2 . Thus the lemma is proven. \square

Theorem. A.2.3. Let $f \in \mathcal{L}_T^2$ be an arbitrary function and $f_{(n)} \in \mathcal{S}_T^2$ a sequence of step functions converging to f . Then there exists a unique, w.p.1, \mathcal{A}_T -measurable random variable $I \in L^2(\Omega, \mathcal{A}, \mathcal{P})$ such that hold:

$$\mathbb{E}\left(|I(f_{(n)}) - I|^2\right) \rightarrow 0 \text{ as } n \rightarrow \infty \tag{94}$$

Proof. The sequence $f_{(n)}$ converges to f , thus the limit for $n \rightarrow \infty$ of the sequence $\int_0^T \mathbb{E}\left(|f_{(n)}(t, \cdot) - f(t, \cdot)|^2\right) dt$ is equal to 0.

The linear property of the Ito integrals and the inequality $(p + q)^2 \leq 2(p^2 + q^2)$ allows the following inequality

$$\begin{aligned}
&\mathbb{E}\left(|I(f_{(n)}) - I(f_{(n+m)})|^2\right) = \mathbb{E}\left(|I(f_{(n)} - f_{(n+m)})|^2\right) \\
&= \int_0^T \mathbb{E}\left(|f_{(n)}(t, \cdot) - f_{(n+m)}(t, \cdot)|^2\right) dt \\
&= \int_0^T \mathbb{E}\left(|(f_{(n)}(t, \cdot) - f(t, \cdot)) + (f(t, \cdot) - f_{(n+m)}(t, \cdot))|^2\right) dt \\
&\leq 2 \int_0^T \mathbb{E}\left(|f_{(n)}(t, \cdot) - f(t, \cdot)|^2\right) \\
&\quad + 2 \int_0^T \mathbb{E}\left(|f(t, \cdot) - f_{(n+m)}(t, \cdot)|^2\right) dt \tag{95}
\end{aligned}$$

Thus $I(f_{(n)})$ is a Cauchy sequence in the Banach space $L^2(\Omega, \mathcal{A}, \mathcal{P})$. Thus there exists a unique, w.p.1, random variable $I \in L^2(\Omega, \mathcal{A}, \mathcal{P})$ such that hold: $\mathbb{E}\left(|I(f_{(n)}) - I|^2\right) \rightarrow 0$ as $n \rightarrow \infty$. The variable I is \mathcal{A}_T -measurable, because it is the limit of a converging sequence of \mathcal{A}_T -measurable random variables.

□

This theorem is not enough. The theorem only indicates that a given converging sequence $f^{(n)}$ has a unique Ito-integral. But it needs to be proven that all the sequences converging to a function f have the same Ito-integral.

Theorem. A.2.4. Let $f \in \mathcal{L}_T^2$ be an arbitrary function and $f_{(n)} \in \mathcal{S}_T^2$ and $g_{(n)} \in \mathcal{S}_T^2$ sequences of step functions converging to f , s.t. $I(f_{(n)})$ converges to I and $I(g_{(n)})$ converges to J . Then holds $I = J$ w.p.1.

Proof. The functions stated in the theorem all converge to a function, thus the limits can be changed to limits inferior. Then we can use the lemma of Fatou.

$$\begin{aligned}
\mathbb{E}\left(\left|I - J\right|^2\right) &= \mathbb{E}\left(\liminf_{n \rightarrow \infty} \left|I(f_{(n)}) - I(g_{(n)})\right|^2\right) \\
&\leq \liminf_{n \rightarrow \infty} \mathbb{E}\left(\left|I(f_{(n)}) - I(g_{(n)})\right|^2\right) \\
&= \liminf_{n \rightarrow \infty} \mathbb{E}\left(\left|I(f_{(n)} - g_{(n)})\right|^2\right) \\
&= \liminf_{n \rightarrow \infty} \int_0^T \mathbb{E}\left(\left|f_{(n)} - g_{(n)}\right|^2\right) dt \\
&= \liminf_{n \rightarrow \infty} \int_0^T \mathbb{E}\left(\left|f_{(n)} - f + f - g_{(n)}\right|^2\right) dt \\
&\leq \liminf_{n \rightarrow \infty} 2 \int_0^T \mathbb{E}\left(\left|f_{(n)} - f\right|^2\right) dt + 2 \int_0^T \mathbb{E}\left(\left|f - g_{(n)}\right|^2\right) dt \\
&= \liminf_{n \rightarrow \infty} 2\mathbb{E}\left(\left|I(f_{(n)}) - I\right|^2\right) dt \\
&\quad + 2\mathbb{E}\left(\left|J - I(g_{(n)})\right|^2\right) dt \tag{96}
\end{aligned}$$

The limit inferior for $n \rightarrow \infty$ now give rise to: $\mathbb{E}\left(\left|I - J\right|^2\right) = 0$ and thus $I = J$ holds w.p.1.

□

The Ito-integral of a function f is now uniquely determined. Thus the Ito-integral can now be defined for functions in \mathcal{L}_T^2 .

Definition. A.2.5. Let $f_{(n)}$ be an arbitrary sequence in \mathcal{L}_T^2 with limit f and with Ito-integral $I(f_{(n)})$ as defined in the previous definition. Then the common mean-square limit of the sequences $I(f_{(n)})$ for all sequences $f_{(n)}$ of step functions in \mathcal{S}_T^2 converging to f is the Ito-integral of f .

It is unclear whether the Ito-integral still exhibits the properties as it does for the step functions.

Theorem. A.2.6. The Ito stochastic integral exhibits the same three properties for functions in \mathcal{L}_T^2 as it does for functions in \mathcal{S}_T^2 .

Proof. The first property follows from the previous two theorems.

The third property follows from the previous two theorems, when they are applied to the function $h = \alpha f + \beta g$ with the step functions $h_{(n)} = \alpha f_{(n)} + \beta g_{(n)}$.

By the application of the previous two theorems is $I(f_n)$ a Cauchy sequence with limit $I(f)$. Thus $I(f_n)^2$ is a Cauchy sequence with limit $I(f)^2$.

With the (reversed) lemma of Fatou, the Fatou-Lebesgue theorem and the fact that all the above stated functions have a limit, we get the following two inequalities:

$$\begin{aligned} \mathbb{E} \left(I(f)^2 \right) &= \mathbb{E} \left(\limsup_{n \rightarrow \infty} I(f_{(n)})^2 \right) \geq \limsup_{n \rightarrow \infty} \mathbb{E} \left(I(f_{(n)})^2 \right) \\ &\geq \liminf_{n \rightarrow \infty} \mathbb{E} \left(I(f_{(n)})^2 \right) = \liminf_{n \rightarrow \infty} \int_0^T \mathbb{E} \left(f_{(n)}^2 \right) dt \\ &\geq \int_0^T \mathbb{E} \left(\liminf_{n \rightarrow \infty} f_{(n)}^2 \right) dt = \int_0^T \mathbb{E} \left(f^2 \right) dt \end{aligned} \quad (97)$$

$$\begin{aligned} \mathbb{E} \left(I(f)^2 \right) &= \mathbb{E} \left(\liminf_{n \rightarrow \infty} I(f_{(n)})^2 \right) \leq \liminf_{n \rightarrow \infty} \mathbb{E} \left(I(f_{(n)})^2 \right) \\ &\leq \limsup_{n \rightarrow \infty} \mathbb{E} \left(I(f_{(n)})^2 \right) = \limsup_{n \rightarrow \infty} \int_0^T \mathbb{E} \left(f_{(n)}^2 \right) dt \\ &\leq \int_0^T \mathbb{E} \left(\limsup_{n \rightarrow \infty} f_{(n)}^2 \right) dt = \int_0^T \mathbb{E} \left(f^2 \right) dt \end{aligned} \quad (98)$$

Thus the second property holds. □

These properties imply the following corollary.

Corollary. A.2.7. Let $f, g \in \mathcal{L}_T^2$ then the following equation hold:

$$\mathbb{E} (I(f) I(g)) = \int_0^T \mathbb{E} (f(t, \cdot) g(t, \cdot)) dt \quad (99)$$

Proof. The second property of the Ito-integral applied to $h = f + g$, f and g in combination with the linearity of the expectation and the Ito-integral justifies the equation. □

The Ito-integral is now defined for \mathcal{L}_T^2 and with all its properties. In this derivation there has been made use of the fact that $(dW_t)^2$ is equal to dt in the mean square sense. Thus the problem can arise that the chain rule of classical calculus is not valid any more. Thus the stochastic counterpart of the chain rule must be derived.

For any derivation can be done, it is necessary to determine the space of the functions. In this case \mathcal{L}_T^ω is used. This is a Lebesgue-measure on $[0, T] \times \Omega$. This means that functions depending on t and ω can be integrated with respect to functions of t and ω .

Let e, f be two functions such that $\sqrt{|e|}, f \in \mathcal{L}_T^\omega$. These functions have the same properties as functions of \mathcal{L}_T^2 . Then hold: $\int_0^T |e(s, \omega)| ds < \infty$ w.p.1

Definition. A.2.8. Let $\sqrt{|e|}, e, f \in \mathcal{L}_T^\omega$, $W = \{W_t(\omega) | t \in [0, t], \omega \in \Omega\}$ be a Wiener process and $X = \{X_t(\omega) | t \in [0, t], \omega \in \Omega\}$ be a stochastic process. Then the stochastic differential is the following equation.

$$dX_t(\omega) = e(t, \omega) dt + f(t, \omega) dW_t(\omega) \quad (100)$$

This is only the symbolic differential notation for the integral equation:

$$X_t(\omega) - X_s(\omega) = \int_s^t e(u, \omega) du + \int_s^t f(u, \omega) dW_u(\omega) \quad (101)$$

w.p.1 for all $0 \leq s \leq t \leq T$. The integrals are Lebesgue or Riemann integral for each $\omega \in \Omega$ and Ito integrals.

The Ito-integral for a function $g \in \mathcal{L}_T^\omega$ has been defined as the limit of the Ito-integrals for functions $g_{(n)} \in \mathcal{L}_T^2$.

For convenience it is assumed that X_t is separable and jointly measurable with almost surely continuous sample paths. When e and f do not depend on t then they are assumed to be \mathcal{A}_0 -measurable random variables.

This implies that for linear combinations of stochastic differentials it is allowed to use the same rules as for the Lebesgue/Riemann and Ito integrals. For non-linear combinations or transformations the Ito Theorem is needed.

Theorem. A.2.9. (Ito) Let $U : [0, T] \times \mathbb{R} \rightarrow \mathbb{R}$ be a function with continuous partial derivatives $\frac{\partial U}{\partial t}$, $\frac{\partial U}{\partial x}$ and $\frac{\partial^2 U}{\partial x^2}$, X_t be as in the previous definition with $\sqrt{|e|}, f \in \mathcal{L}_T^\omega$ and $Y_t = U(t, X_t)$ for $0 \leq t \leq T$. Then holds w.p.1 for any $0 \leq s \leq t \leq T$:

$$\begin{aligned} Y_t - Y_s &= \int_s^t \left\{ \frac{\partial U}{\partial t}(u, X_u) + e_u \frac{\partial U}{\partial x}(u, X_u) \right. \\ &\quad \left. + \frac{1}{2} f_u^2 \frac{\partial^2 U}{\partial x^2}(u, X_u) \right\} du + \int_s^t f_u \frac{\partial U}{\partial x}(u, X_u) dW_u \end{aligned} \quad (102)$$

Proof. The rigorous proof of this theorem will not be given here. A sketch of the proof will be given below. The rigorous proof can be found on pages 92-95 of Kloeden & Platen.

Let us use the notation $x(t) = X_t$ and let dt be an infinitesimal increase in time, then we can use the Taylor approximation of Y_t with respect to t .

$$Y_s = Y_{t_0} + dt \frac{dY_t}{dt}(t_0) + dt^2 \frac{d^2 Y_t}{dt^2}(t_0) + \mathcal{O}(dt^3) \quad (103)$$

The Taylor series can only be used when Y is infinitely differentiable. This is not the case because a Wiener process is part of X_t and thus X_t is not differentiable.

Directly from U we can use partial differentiation to make a distinction between t and X_t . Therefore

$$\begin{aligned}
dY &= dU(t, x(t)) \\
&= \frac{\partial U(t, x(t))}{\partial t} dt + \frac{\partial U(t, x(t))}{\partial x(t)} dx(t) \\
&+ \frac{1}{2} \frac{\partial^2 U(t, x(t))}{\partial t^2} dt^2 + \frac{1}{2} \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} dx(t)^2 + \mathcal{O}(dt^3, dx(t)^3) \\
&= \frac{\partial U(t, x(t))}{\partial t} dt + \frac{\partial U(t, x(t))}{\partial x(t)} [e(t) dt + f(t) dW_t] \\
&+ \frac{1}{2} \frac{\partial^2 U(t, x(t))}{\partial t^2} dt^2 + \frac{1}{2} \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} [e(t) dt + f(t) dW_t]^2 \\
&+ \mathcal{O}(dt^3, dx(t)^3) \\
&= \frac{\partial U(t, x(t))}{\partial t} dt + \frac{\partial U(t, x(t))}{\partial x(t)} [e(t) dt + f(t) dW_t] + \frac{1}{2} \frac{\partial^2 U(t, x(t))}{\partial t^2} dt^2 \\
&+ \frac{1}{2} \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} [e(t)^2 dt^2 + 2e(t)f(t) dt dW_t + f(t)^2 dW_t^2] \\
&+ \mathcal{O}(dt^3, dt^2 dW_t, dt dW_t^2, dW_t^3) \\
&= \left[\frac{\partial U(t, x(t))}{\partial t} + e(t) \frac{\partial U(t, x(t))}{\partial x(t)} \right] dt + f(t) \frac{\partial U(t, x(t))}{\partial x(t)} dW_t \\
&+ \left[\frac{1}{2} \frac{\partial^2 U(t, x(t))}{\partial t^2} + \frac{1}{2} e(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} \right] dt^2 \\
&+ e(t)f(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} dt dW_t + \frac{1}{2} f(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} dW_t^2 \\
&+ \mathcal{O}(dt^3, dt^2 dW_t, dt dW_t^2, dW_t^3) \tag{104}
\end{aligned}$$

To get to the correct derivation we must use the fact that for $dx(t)$ we have to use the norm $\|f(t, \cdot)\|_{2,T}^2 = \int_0^T \mathbb{E}(f(t, \cdot)^2) dt$ applied to X_t in Y_t . Thus when this norm is applied to the X_t part of Y_t we get that the dW_t part will be of norm \sqrt{dt} . Therefore this term influences Y_t in the norm of t , but cannot be integrated with the Lebesgue integral. Therefore dW_t remains and an Ito integral is necessary. Meanwhile the dW_t^2 term in X_t will, because of the norm of W_t ($\|\cdot\|_{2,T}$) applied to X_t , be of norm dt , which can be Lebesgue integrated. Therefore dW_t^2 has to be replaced by dt . Applying these changes to equation (104) we get

$$\begin{aligned}
dY &= \left[\frac{\partial U(t, x(t))}{\partial t} + e(t) \frac{\partial U(t, x(t))}{\partial x(t)} \right] dt + f(t) \frac{\partial U(t, x(t))}{\partial x(t)} dW_t \\
&+ \left[\frac{1}{2} \frac{\partial^2 U(t, x(t))}{\partial t^2} + \frac{1}{2} e(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} \right] dt^2 \\
&+ e(t)f(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} dt dW_t + \frac{1}{2} f(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} dW_t^2 \\
&+ \mathcal{O}(dt^3, dt^2 dW_t, dt dW_t^2, dW_t^3) \\
&= \left[\frac{\partial U(t, x(t))}{\partial t} + e(t) \frac{\partial U(t, x(t))}{\partial x(t)} \right] dt + f(t) \frac{\partial U(t, x(t))}{\partial x(t)} dW_t \\
&+ \left[\frac{1}{2} \frac{\partial^2 U(t, x(t))}{\partial t^2} + \frac{1}{2} e(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} \right] dt^2
\end{aligned}$$

$$\begin{aligned}
& + e(t) f(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} dt dW_t + \frac{1}{2} f(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} dt \\
& + \mathcal{O}(dt^3, dt^2 dW_t, dt^2, dt dW_t) \\
& = \left[\frac{\partial U(t, x(t))}{\partial t} + e(t) \frac{\partial U(t, x(t))}{\partial x(t)} + \frac{1}{2} f(t)^2 \frac{\partial^2 U(t, x(t))}{\partial x(t)^2} \right] dt \\
& + f(t) \frac{\partial U(t, x(t))}{\partial x(t)} dW_t + \mathcal{O}(dt^2, dt dW_t). \tag{105}
\end{aligned}$$

Formally it can be proven that the higher order terms vanish. Then applying Lebesgue and Ito integrals will now give (103). □

Until this point we have only defined the Ito-integral for scalar functions and variables. For very basic physical and mathematical problems it is necessary to have the same theory for vector functions and variables.

A.2.1 Vector Ito-integrals and Vector Ito theorem

For the definition of Ito-integrals of vector functions and parameters it is convenient to define it in terms of scalar Ito-integrals. To do this properly we have to introduce the vectorial counterparts of the scalar mathematical objects.

Definition. A.2.10 An n -dimensional Wiener process with independent components associated with an increasing family of sigma-algebras $\{\mathcal{A}_t, t \geq 0\}$ is a process $W = \{W_t = (W_t^1, W_t^2, \dots, W_t^n), t \geq 0\}$ where W^i for $i = 1, 2, \dots, n$ are scalar Wiener processes with respect to $\{\mathcal{A}_t, t \geq 0\}$, which are pairwise independent and with components W_t^i that follow four properties

1. W_t^i is \mathcal{A}_t -measurable
2. $\mathbb{E}(W_t^i | \mathcal{A}_0) = 0$ w.p.1
3. $\mathbb{E}(W_t^i - W_s^i | \mathcal{A}_s) = 0$ w.p.1
4. $\mathbb{E}\left((W_t^i - W_s^i)(W_t^j - W_s^j) | \mathcal{A}_s\right) = (t - s) \delta_{i,j}$ w.p.1

for $0 \leq s \leq t$ and $i, j = 1, 2, \dots, n$ and where $\delta_{i,j}$ denotes the Kronecker delta.

Definition. A.2.11 Let $e : [0, T] \times \Omega \rightarrow \mathbb{R}^d$ with components e^k satisfying $\sqrt{|e^k|} \in \mathcal{L}_T^\omega$ (or \mathcal{L}_T^2) for $k = 1, 2, \dots, d$ be a d -dimensional vector function and let $F : [0, T] \times \Omega \rightarrow \mathbb{R}^{d \times n}$ with components $F^{i,j} \in \mathcal{L}_T^\omega$ (or \mathcal{L}_T^2) for $i = 1, 2, \dots, d$ and $j = 1, 2, \dots, n$ be an $d \times n$ -matrix function then a d -dimensional vector stochastic integral equation for any $0 \leq s \leq t$ is

$$X_t - X_s = \int_s^t e_r dr + \int_s^t F_r dW_r \tag{106}$$

with e_t, F_t denote the vector and matrix functions e, F respectively at time t and X_t denotes a stochastic process X at time t , which is interpreted as

$$X_t^i - X_s^i = \int_s^t e_r^i dr + \sum_{j=1}^n \int_s^t F_r^{i,j} dW_r^j \quad w.p.1 \quad (107)$$

with $i = 1, 2, \dots, d$. Then the first integral equation is symbolically denoted as a d -dimensional vector stochastic differential equation

$$dX_t = e_t dt + F_t dW_t. \quad (108)$$

Remark that for $d = 1$ the defined process is a scalar process with multiple independent noise processes. With the definition of the new process X it is now possible to state the Ito theorem for vector processes.

Theorem. *A.2.12 (Vector Ito)* Let X be a stochastic process defined by equation (77) and let $U : [0, T] \times \mathbb{R}^d \rightarrow \mathbb{R}$ have continuous partial derivatives $\frac{\partial U}{\partial t}, \frac{\partial U}{\partial x_i}, \frac{\partial^2 U}{\partial x_i \partial x_j}$ for $i, j = 1, 2, \dots, d$ and define a scalar stochastic process $Y = \{Y_t, 0 \leq t \leq T\}$ by

$$\begin{aligned} Y_t &= U(t, X_t) \\ &= U(t, X_t^1, X_t^2, \dots, X_t^d) \end{aligned} \quad w.p.1, \quad (109)$$

then the stochastic differential for Y_t is given by

$$\begin{aligned} dY_t &= \left[\frac{\partial U}{\partial t} + \sum_{i=1}^d e_t^i \frac{\partial U}{\partial x_i} + \frac{1}{2} \sum_{j=1}^n \sum_{i,k=1}^d F_t^{k,j} F_t^{i,j} \frac{\partial^2 U}{\partial x_k \partial x_i} \right] dt \\ &+ \sum_{j=1}^n \sum_{k=1}^d F_t^{k,j} \frac{\partial U}{\partial x_k} dW_t^j \\ &= \left[\frac{\partial U}{\partial t} + e_t^\top \nabla U + \frac{1}{2} \text{tr} (F_t F_t^\top H_x U) \right] dt + \nabla U^\top F_t dW_t \end{aligned} \quad (110)$$

with all the partial derivatives evaluated at (t, X_t) and H_x the Hessian matrix containing only the spatial second derivatives.

Proof. The rigorous proof is not given since it is a straightforward modification of the rigorous proof of A.2.9.

For the sketch of the proof modify in the sketch of the proof of A.2.9. $dx(t) = e(t) dt + f(t) dW_t$ with $dx_i(t) = e^i(t) dt + \sum_{j=1}^m F^{i,j}(t) dW_t^j$. Modify in equation (74) in the second line the differentiation to the scalar x with the multi-variable differentiation with respect to the components of x . After these modifications follow the proof of A.2.9. and modify where necessary. The result will be (110). □

A.3 Stochastic Differential Equations

Numerous processes in nature behave with an underlying stochastic process. This is often because of particles at a very small scale such that at large scales the collective behaviour of the particles are governed by the rules of probability theory. Most of the time this behaviour can be seen as a general relationship with noise. The noise can be seen as the manifestation of the rules of probability on the collective behaviour of the particles.

Most processes in nature are only described by the general relationship. This relationship can be a differential equation. But when you know there will be noise, then you want to incorporate the noise into the description of the process. Normally differential equations are enough. But for Gaussian noise, also known as white noise, you need a Wiener process. In section A.1 Wiener processes are introduced together with its properties. The most important property is that a Wiener process is nowhere differentiable. Thus differential equations can not be used as a description. Integral equations can do the same job, but do not pose the restriction of differentiability on a Wiener process.

In section A.2 it is argued that normal integrals cannot be used. Ito-integrals were created to do the job. Thus integral equations can be used for a description. The notation will still be that of differential equations, but it must be read as integral equations.

Definition. *A.3.1. Let a, b be functions of \mathbb{L}^2 , X_t a stochastic process dependent on $t \in [0, T]$ and $W = \{W_t | t \in [0, t]\}$ a Wiener process, then the form of a stochastic differential equation is:*

$$dX_t = a(t, X_t) dt + b(t, X_t) dW_t \quad (111)$$

This is not easy to solve. But a certain set of differential equations can be very easy to solve:

Definition. *A.3.2. Let a, b be functions of \mathbb{L}^2 , X_t a stochastic process dependent on $t \in [0, T]$, $W = \{W_t | t \in [0, t]\}$ a Wiener process, and $dX_t = a(t, X_t) dt + b(t, X_t) dW_t$ is a stochastic differential equation and $\underline{a}(t, x)$ be equal to $a(t, x) - \frac{1}{2}b(t, x) \frac{\partial b}{\partial x}(t, x)$, then the Stratonovich stochastic differential equation is*

$$dX_t = \underline{a}(t, X_t) dt + b(t, X_t) \circ dW_t \quad (112)$$

The later differential equation is an integral equation with a Stratonovich integral. It is just like an Ito-integral, but it has the property that the integral rules of classical calculus apply. Thus the solution can be received without difficult calculations.

For the non-linear case this can solve the equation. Otherwise there sometimes is a function $U(t, x)$ such that with the Ito theorem the non-linear SDE can be transformed into a linear SDE. If then this SDE is solved, the reversed transformation will give the appropriate solution to the non-linear SDE.

This can only be done if a linear SDE can be solved. First a few results from calculus will be derived.

Lemma. A.3.3. Let X_t be a time dependent process, a be a function in \mathcal{L}_T^2 then the ordinary differential equation $dX_t = a(t) X_t dt$ has the fundamental solution

$$\Phi_{t,t_0} = e^{\int_{t_0}^t a(s) ds} . \quad (113)$$

Proof. The proof is a simple calculations by filling in the fundamental solution and applying the fundamental theorem of calculus.

$$\frac{d\Phi_{t,t_0}}{dt} = \frac{e^{\int_{t_0}^t a(s) ds}}{dt} = e^{\int_{t_0}^t a(s) ds} \frac{d \int_{t_0}^t a(s) ds}{dt} = \Phi_{t,t_0} \frac{d \int_{t_0}^t a(s) ds}{dt} = \Phi_{t,t_0} a(t) \quad (114)$$

$$\Phi_{t_0,t_0} = e^{\int_{t_0}^{t_0} a(s) ds} = e^0 = 1 \quad (115)$$

Thus equation (83) is the fundamental solution of the differential equation. □

The general linear scalar SDE is defined as

$$dX_t = [a(t) X_t + b(t)] dt + [c(t) X_t + d(t)] dW_t \quad (116)$$

with $a, b, c, d \in \mathcal{L}_T^2$.

Theorem. A.3.4 Let X_t be a time dependent stochastic process defined by (86). Then the solution of this stochastic differential equation is equal to

$$\begin{aligned} X_t = & e^{\int_{t_0}^t [a(s) - \frac{1}{2}c(s)^2] ds + \int_{t_0}^t c(s) dW_s} \left[X_{t_0} + \right. \\ & + \int_{t_0}^t [b(s) - c(s) d(s)] e^{\int_{t_0}^s [\frac{1}{2}c(r)^2 - a(r)] dr - \int_{t_0}^s c(r) dW_r} ds + \\ & \left. + \int_{t_0}^t d(s) e^{\int_{t_0}^s [\frac{1}{2}c(r)^2 - a(r)] dr - \int_{t_0}^s c(r) dW_r} dW_s \right] \quad (117) \end{aligned}$$

Proof. Let $\Phi_{t,t_0} = e^{\int_{t_0}^t [a(s) - \frac{1}{2}c(s)^2] ds + \int_{t_0}^t c(s) dW_s}$ hold and

$$\begin{aligned} U = & X_{t_0} + \\ & + \int_{t_0}^t [b(s) - c(s) d(s)] e^{\int_{t_0}^s [\frac{1}{2}c(r)^2 - a(r)] dr - \int_{t_0}^s c(r) dW_r} ds + \\ & + \int_{t_0}^t d(s) e^{\int_{t_0}^s [\frac{1}{2}c(r)^2 - a(r)] dr - \int_{t_0}^s c(r) dW_r} dW_s \end{aligned}$$

$$= X_{t_0} + \int_{t_0}^t [b(s) - c(s) d(s)] \Phi_{s,t_0}^{-1} ds + \int_{t_0}^t d(s) \Phi_{s,t_0}^{-1} dW_s \quad (118)$$

hold, then $X_t = U\Phi_{t,t_0}$ holds. Applying the vector Ito theorem on $X_t = V(t, U, \Phi_{t,t_0})$ we get

$$\begin{aligned} dX_t &= \left[\frac{\partial V}{\partial U} \frac{\partial U}{\partial t} + \frac{\partial V}{\partial \Phi_{t,t_0}} \frac{\partial \Phi_{t,t_0}}{\partial t} + \frac{1}{2} \left(\frac{\partial U}{\partial W_t} \right)^2 \frac{\partial^2 V}{\partial U^2} + \frac{\partial \Phi_{t,t_0}}{\partial W_t} \frac{\partial U}{\partial W_t} \frac{\partial^2 V}{\partial U \partial \Phi_{t,t_0}} + \right. \\ &+ \left. \frac{1}{2} \left(\frac{\partial \Phi_{t,t_0}}{\partial W_t} \right)^2 \frac{\partial^2 V}{\partial \Phi_{t,t_0}^2} \right] dt + \left[\frac{\partial U}{\partial W_t} \frac{\partial V}{\partial U} + \frac{\partial \Phi_{t,t_0}}{\partial W_t} \frac{\partial V}{\partial \Phi_{t,t_0}} \right] dW_t \\ &= \left[U \left(a(t) - \frac{1}{2} c(t)^2 \right) \Phi_{t,t_0} + \Phi_{t,t_0} (b(t) - c(t) d(t)) \Phi_{t,t_0}^{-1} \right. \\ &+ \left. \Phi_{t,t_0} c(t) d(t) \Phi_{t,t_0}^{-1} + \frac{1}{2} U \phi_{t,t_0} c(t)^2 \right] dt \\ &+ \left[\Phi_{t,t_0} d(t) \Phi_{t,t_0}^{-1} + U c(t) \Phi_{t,t_0} \right] dW_t \\ &= [a(t) U \Phi_{t,t_0} + b(t)] dt + [c(t) U \Phi_{t,t_0} + d(t)] dW_t \\ &= [a(t) X_t + b(t)] dt + [c(t) X_t + d(t)] dW_t. \end{aligned} \quad (119)$$

Thus (117) is a solution of (116). □

An example can now be given how to solve a non-linear SDE with the help of a transformation function U .

Example. *A.3.5. Stochastic Verhulst equation.* Let X_t be a stochastic process, W_t a Wiener process and $\lambda, \sigma \in \mathcal{L}^2$, then the stochastic Verhulst equation is defined as

$$dX_t = [\lambda X_t - X_t^2] dt + \sigma X_t dW_t \quad (120)$$

The solution can be derived quite easily with the appropriate transformation $Y_t = U(t, X_t) = \frac{1}{X_t}$. According to the Ito theorem the differential equation for Y_t is equal to

$$\begin{aligned} dY_t &= \left[\frac{\partial U}{\partial t} + \frac{\partial U}{\partial X_t} \frac{\partial X_t}{\partial t} + \frac{1}{2} \left(\frac{\partial X_t}{\partial W_t} \right)^2 \frac{\partial^2 U}{\partial X_t^2} \right] dt + \left[\frac{\partial U}{\partial X_t} \frac{\partial X_t}{\partial W_t} \right] dW_t \\ &= \left[-\frac{1}{X_t^2} (\lambda X_t - X_t^2) + \frac{1}{2} \sigma^2 X_t^2 \frac{2}{X_t^3} \right] dt - \frac{1}{X_t^2} \sigma X_t dW_t \\ &= \left[-\lambda \frac{1}{X_t} + 1 + \sigma^2 \frac{1}{X_t} \right] dt - \sigma \frac{1}{X_t} dW_t \\ &= [(\sigma^2 - \lambda) Y_t + 1] dt - \sigma Y_t dW_t \end{aligned} \quad (121)$$

The SDE is now in a linear form, thus we can apply solution (117).

$$\begin{aligned}
X_t &= \frac{1}{Y_t} \\
&= \frac{1}{e^{\int_{t_0}^t [\sigma^2 - \lambda - \frac{1}{2}\sigma^2] ds - \int_{t_0}^t \sigma dW_s} \left[\frac{1}{X_{t_0}} + \int_{t_0}^t e^{\int_{t_0}^s [\frac{1}{2}\sigma^2 - \sigma^2 + \lambda] dr + \int_{t_0}^s \sigma dW_r} ds \right]} \\
&= \frac{e^{\int_{t_0}^t [\lambda - \frac{1}{2}\sigma^2] ds + \int_{t_0}^t \sigma dW_s}}{\frac{1}{X_{t_0}} + \int_{t_0}^t e^{\int_{t_0}^s [\lambda - \frac{1}{2}\sigma^2] dr + \int_{t_0}^s \sigma dW_r} ds} \\
&= \frac{X_{t_0} e^{\int_{t_0}^t [\lambda - \frac{1}{2}\sigma^2] ds + \int_{t_0}^t \sigma dW_s}}{1 + X_{t_0} \int_{t_0}^t e^{\int_{t_0}^s [\lambda - \frac{1}{2}\sigma^2] dr + \int_{t_0}^s \sigma dW_r} ds} \\
&= \frac{X_{t_0} e^{[\lambda - \frac{1}{2}\sigma^2](t-t_0) + \sigma(W_t - W_{t_0})}}{1 + X_{t_0} \int_{t_0}^t e^{[\lambda - \frac{1}{2}\sigma^2](s-t_0) + \sigma(W_s - W_{t_0})} ds} \tag{122}
\end{aligned}$$

Thus (122) is the solution of (120). The result could only be given because of the Ito theorem and the existence of a solution of the general linear stochastic differential equation.

The solution given in this example can be dependent on the Wiener process, therefore it is needed to introduce more definitions around solutions.

Definition. A.3.6. Let $t \in \mathbb{R}^+$, $\sqrt{|e|}$, $f \in \mathcal{L}_T^\omega$, $W = \{W_t, t \in \mathbb{R}^+\}$ a Wiener process and $X = \{X_t, t \in \mathbb{R}\}$ a stochastic process determined by

$$\begin{aligned}
dX_t &= e(t, \cdot) dt + f(t, \cdot) dW_t \\
&= \begin{cases} a(t, X_t) dt + b(t, X_t) dW_t & t_0 \leq t \leq T \\ 0 & 0 \leq t \leq t_0 \end{cases} \tag{123}
\end{aligned}$$

with $a, b : [t_0, T] \times \mathbb{R} \rightarrow \mathbb{R}$ which are jointly measurable, have a Lipschitz condition, a linear growth bound for $t \in [t_0, T]$ and nonanticipativeness with respect to the given Wiener process, then $X = \{X_t, t \in \mathbb{R}\}$ is called a solution of (123).

The definition of solution was implicitly already used when Ito-integrals and SDE's were defined and constructed. The existence of solutions are normally assumed. The existence of solutions can depend on the Wiener process. This allows for new definitions.

Definition. A.3.7. A SDE has a strong solution if for every Wiener process there exists a solution of the SDE.

Definition. A.3.8. A SDE has a weak solution if there exists a solution of the SDE when only the coefficients are specified, but not the Wiener process.

For solutions to be useful it is necessary to have a notion of uniqueness of solutions.

Definition. A.3.9. Two solutions X_t, Y_t are pathwise unique on $[t_0, T]$ if they satisfy

$$\mathbb{P} \left(\sup_{t_0 \leq t \leq T} |X_t - Y_t| > 0 \right) = 0. \quad (124)$$

Solutions can now be showed to be pathwise unique. The use of integrals and expectations for strong solutions one needs the theorem of Fubini. This theorem needs a solution to be bounded in measure. Sufficient is the existence of a solution bounded in the norm $\|\cdot\|_{2,T}$.

Theorem. A.3.10. Let a SDE be like (123) with the same conditions on a, b . If X_t exhibits the property $\mathbb{E}(|X_{t_0}|^2) < \infty$, then there exists a pathwise unique strong solution X_t on $[t_0, T]$ with the property

$$\sup_{t_0 \leq t \leq T} \mathbb{E}(|X_t|^2) < \infty. \quad (125)$$

Proof. The proof is long and technical. The proof can be found on pages 131-134 of Kloeden & Platen. □

A.3.1 Vector stochastic differential equations

The definitions and solutions defined for the scalar stochastic differential equations are not enough. In many applications it is necessary to be able to do the same with vectors.

Definition. A.3.11. Let $W = \{W_t, t \geq 0\} = \{W_t^1, W_t^2, \dots, W_t^m; t \geq 0\}$ be an m -dimensional Wiener process of which the components W_t^i are independent scalar Wiener processes with respect to a family of σ -algebras, $a : [t_0, T] \times \mathbb{R}^d \rightarrow \mathbb{R}^d$ a d -dimensional vector function, $b : [t_0, T] \times \mathbb{R}^d \rightarrow \mathbb{R}^{d \times m}$ a $d \times m$ -dimensional matrix function, then the d -dimensional vector stochastic differential equation of stochastic process X_t is defined as

$$dX_t = a(t, X_t) dt + b(t, X_t) dW_t. \quad (126)$$

This differential equation is interpreted as the stochastic integral equation

$$X_t = X_{t_0} + \int_{t_0}^t a(s, X_s) ds + \int_{t_0}^t b(s, X_s) dW_s \quad (127)$$

and which is defined as

$$X_t^i = X_{t_0}^i + \int_{t_0}^t a^i(s, X_s) ds + \sum_{j=1}^m \int_{t_0}^t b^{i,j}(s, X_s) dW_s^j \quad (128)$$

Corollary. *The definitions of strong solution, weak solution and pathwise uniqueness for vectors follow from the scalar versions, when applied to all the components of the vector stochastic process X_t . The vector Ito theorem was defined only for scalar processes depending on vector sub-processes. Therefore the vector Ito theorem of vector processes depending on vector sub-processes is defined component-wise.*

The existence of a vector Ito theorem of vector processes depending on vector sub-processes give rise to the idea that non-linear vector SDEs can be transformed into linear vector SDEs. To make this idea work it is necessary to have a solution of the general vector linear SDE.

Definition. *A.3.12. Let X_t be a d -dimensional stochastic process and W_t an m -dimensional Wiener process with independent components equal to scalar Wiener processes, then a d -dimensional linear stochastic differential equation is*

$$dX_t = (A(t) X_t + b(t)) dt + \sum_{i=1}^m (C^i(t) X_t + d^i(t)) dW_t^i \quad (129)$$

with b a d -dimensional vector function, A a $d \times d$ -dimensional matrix function, d a $d \times m$ -dimensional matrix function and C a $d \times d \times m$ -dimensional tensor function.

Theorem. *A.3.13. Let X_t be a stochastic process defined by (129). Then the solution of (129) is*

$$\begin{aligned} X_t &= \Phi_{t,t_0} \left(X_{t_0} + \int_{t_0}^t \Phi_{s,t_0}^{-1} \left[b(s) - \sum_{i=1}^m C^i(s) d^i(s) \right] ds \right. \\ &\quad \left. + \sum_{i=1}^m \int_{t_0}^t \Phi_{s,t_0}^{-1} d^i(s) dW_s^i \right) \end{aligned} \quad (130)$$

with Φ_{t,t_0} the $d \times d$ -dimensional fundamental matrix solution such that $\Phi_{t_0,t_0} = I_d$ and satisfies the matrix differential equation

$$d\Phi_{t,t_0} = A(t) \Phi_{t,t_0} dt + \sum_{i=1}^m C^i(t) \Phi_{t,t_0} dW_t^i \quad (131)$$

which has to be evaluated column vector by column vector.

Proof. Let X_t be $\Phi_{t,t_0} U$, then the Ito theorem can be applied to $X_t = V(\Phi_{t,t_0}^1, \Phi_{t,t_0}^2, \dots, \Phi_{t,t_0}^d, U^1, U^2, \dots, U^d)$. To apply this theorem correctly it is necessary to give the correct equations of (130) and (131) for the components.

$$\begin{aligned} X_t^i &= \sum_{j=1}^d \Phi_{t,t_0}^{i,j} \left(X_{t_0}^j + \int_{t_0}^t \sum_{k=1}^d (\Phi_{s,t_0}^{-1})^{j,k} \left[b^k(s) - \sum_{l=1}^m \sum_{n=1}^d C^{k,n,l}(s) d^{n,l}(s) \right] ds \right. \\ &\quad \left. + \sum_{l=1}^m \int_{t_0}^t \sum_{k=1}^d (\Phi_{s,t_0}^{-1})^{j,k} d^{k,l}(s) dW_s^l \right) \end{aligned} \quad (132)$$

$$d\Phi_{t,t_0}^{i,j} = \left[\sum_{k=1}^d A(t)^{i,k} \Phi_{t,t_0}^{k,j} \right] dt + \sum_{l=1}^m \left[\sum_{k=1}^d C^{i,k,l}(t) \Phi_{t,t_0}^{k,j} \right] dW_t^l \quad (133)$$

Now it possible to show that X_t^i satisfies the component version of (129).

$$\begin{aligned} dX_t^i &= d \left(\sum_{j=1}^d \Phi_{t,t_0}^{i,j} U^j \right) = \left[\sum_{j=1}^d \left(\frac{\partial V}{\partial \Phi_{t,t_0}^{i,j}} \frac{\partial \Phi_{t,t_0}^{i,j}}{\partial t} + \frac{\partial V}{\partial U^j} \frac{\partial U^j}{\partial t} \right) \right. \\ &+ \frac{1}{2} \sum_{j,k=1}^d \sum_{l=1}^m \frac{\partial \Phi_{t,t_0}^{i,j}}{\partial W_t^l} \frac{\partial \Phi_{t,t_0}^{i,k}}{\partial W_t^l} \frac{\partial^2 V}{\partial \Phi_{t,t_0}^{i,j} \partial \Phi_{t,t_0}^{i,k}} \\ &+ \frac{1}{2} \sum_{j,k=1}^d \sum_{l=1}^m \frac{\partial \Phi_{t,t_0}^{i,j}}{\partial W_t^l} \frac{\partial U^k}{\partial W_t^l} \frac{\partial^2 V}{\partial \Phi_{t,t_0}^{i,j} \partial U^k} \\ &+ \frac{1}{2} \sum_{j,k=1}^d \sum_{l=1}^m \frac{\partial U^j}{\partial W_t^l} \frac{\partial \Phi_{t,t_0}^{i,k}}{\partial W_t^l} \frac{\partial^2 V}{\partial U^j \partial \Phi_{t,t_0}^{i,k}} \\ &+ \left. \frac{1}{2} \sum_{j,k=1}^d \sum_{l=1}^m \frac{\partial U^j}{\partial W_t^l} \frac{\partial U^k}{\partial W_t^l} \frac{\partial^2 V}{\partial U^j \partial U^k} \right] dt \\ &+ \sum_{l=1}^m \sum_{j=1}^d \left[\frac{\partial \Phi_{t,t_0}^{i,j}}{\partial W_t^l} \frac{\partial V}{\partial \Phi_{t,t_0}^{i,j}} + \frac{\partial U^j}{\partial W_t^l} \frac{\partial V}{\partial U^j} \right] dW_t^l \\ &= \sum_{j=1}^d \left[U^j \frac{\partial \Phi_{t,t_0}^{i,j}}{\partial t} + \Phi_{t,t_0}^{i,j} \frac{\partial U^j}{\partial t} + \sum_{l=1}^m \frac{\partial U^j}{\partial W_t^l} \frac{\partial \Phi_{t,t_0}^{i,j}}{\partial W_t^l} \right] dt \\ &+ \sum_{l=1}^m \sum_{j=1}^d \left[U^j \frac{\partial \Phi_{t,t_0}^{i,j}}{\partial W_t^l} + \Phi_{t,t_0}^{i,j} \frac{\partial U^j}{\partial W_t^l} \right] dW_t^l \\ &= \sum_{j=1}^d \left[U^j \left[\sum_{k=1}^d A(t)^{i,k} \Phi_{t,t_0}^{k,j} \right] + \Phi_{t,t_0}^{i,j} \left[\sum_{k=1}^d (\Phi_{t,t_0}^{-1})^{j,k} \right. \right. \\ &\times \left. \left. \left[b^k(t) - \sum_{l=1}^m \sum_{n=1}^d C^{k,n,l}(t) d^{n,l}(t) \right] \right] + \sum_{l=1}^m \left[\sum_{k=1}^d C^{i,k,l}(t) \Phi_{t,t_0}^{k,j} \right. \right. \\ &\times \left. \left. \left[\sum_{n=1}^d (\Phi_{t,t_0}^{-1})^{j,n} d^{n,l}(t) \right] \right] \right] dt \\ &+ \sum_{l=1}^m \sum_{j=1}^d \left[U^j \left[\sum_{k=1}^d C^{i,k,l}(t) \Phi_{t,t_0}^{k,j} \right] + \Phi_{t,t_0}^{i,j} \left[\sum_{n=1}^d (\Phi_{t,t_0}^{-1})^{j,n} d^{n,l}(t) \right] \right] dW_t^l \\ &= \left[\sum_{k=1}^d A(t)^{i,k} \sum_{j=1}^d \Phi_{t,t_0}^{k,j} U^j + \sum_{k=1}^d \left(\sum_{j=1}^d \Phi_{t,t_0}^{i,j} (\Phi_{t,t_0}^{-1})^{j,k} \right) \right. \\ &\times \left. \left(b^k(t) - \sum_{l=1}^m \sum_{n=1}^d C^{k,n,l}(t) d^{n,l}(t) \right) + \sum_{l=1}^m \sum_{k=1}^d \sum_{n=1}^d C^{i,k,l}(t) d^{n,l}(t) \right. \\ &\times \left. \sum_{j=1}^d \Phi_{t,t_0}^{k,j} (\Phi_{t,t_0}^{-1})^{j,n} \right] dt + \sum_{l=1}^m \left[\left(\sum_{k=1}^d C^{i,k,l}(t) \sum_{j=1}^d \Phi_{t,t_0}^{k,j} U^j \right) \right. \end{aligned}$$

$$\begin{aligned}
& + \left(\sum_{n=1}^d \sum_{j=1}^d \Phi_{t,t_0}^{i,j} (\Phi_{t,t_0}^{-1})^{j,n} d^{n,l}(t) \right) dW_t^l \\
& = \left[\sum_{k=1}^d A(t)^{i,k} X_t^k + b^i(t) - \sum_{l=1}^m \sum_{n=1}^d C^{i,n,l}(t) d^{n,l}(t) \right. \\
& + \left. \sum_{l=1}^m \sum_{k=1}^d C^{i,k,l}(t) d^{k,l}(t) \right] dt + \sum_{l=1}^m \left[\left(\sum_{k=1}^d C^{i,k,l}(t) X_t^k \right) + d^{i,l}(t) \right] dW_t^l \\
& = \left[\left(\sum_{k=1}^d A(t)^{i,k} X_t^k \right) + b^i(t) \right] dt \\
& + \sum_{l=1}^m \left[\left(\sum_{k=1}^d C^{i,k,l}(t) X_t^k \right) + d^{i,l}(t) \right] dW_t^l \tag{134}
\end{aligned}$$

The last line is the component form of differential equation (129). Thus (130) is the solution of (129). \square

The validity of this proof relies on the existence of the matrix Φ_{t,t_0} . A priori it is not known that such a matrix exist.

Lemma. *A.3.14. Let Φ_{t,t_0} be defined as in A.3.13. If the exponent commutate in time for all moments in $[t_0, t]$, then*

$$\Phi_{t,t_0} = \Phi_{t_0,t_0} e^{\int_{t_0}^t A(s) - \sum_{l=1}^m \frac{1}{2} C^l(s) C^l(s) ds + \sum_{l=1}^m \int_{t_0}^t C^l(s) dW_t^l} \tag{135}$$

is the solution of (131).

Proof. Let Φ_{t,t_0} be equal to $\Phi_{t_0,t_0} e^U$, with

$$U = \int_{t_0}^t A(s) - \sum_{l=1}^m \frac{1}{2} C^l(s) C^l(s) ds + \sum_{l=1}^m \int_{t_0}^t C^l(s) dW_t^l \tag{136}$$

Remark that the condition of the commutating exponent in time for all moments in $[t_0, t]$ means that the integral in the exponent can be split into two integrals of $[t_0, t_1]$ and $[t_1, t]$. According to properties of integrals, this should not influence the answer. However if it does not commutate, then the two are not equal, due to the definition of matrix exponentials in terms of Taylor series. Therefore the condition will guarantee the usual properties of integrals. Now it is possible to apply the component version of the Ito theorem.

$$\begin{aligned}
d\Phi_{t,t_0} & = \left[\frac{\partial \Phi_{t,t_0}}{\partial U} \frac{\partial U}{\partial t} - \sum_{l=1}^m \frac{1}{2} \left(\frac{\partial U}{\partial W_t^l} \frac{\partial U}{\partial W_t^l} \frac{\partial^2 \Phi_{t,t_0}}{\partial U^2} \right) \right] dt \\
& + \sum_{l=1}^m \frac{\partial U}{\partial W_t^l} \frac{\partial \Phi_{t,t_0}}{\partial U} dW_t^l \\
& = \left[\Phi_{t_0,t_0} e^U \frac{\partial U}{\partial t} - \sum_{l=1}^m \frac{1}{2} \left(\frac{\partial U}{\partial W_t^l} \right)^2 \Phi_{t_0,t_0} e^U \right] dt
\end{aligned}$$

$$\begin{aligned}
& + \sum_{l=1}^m \frac{\partial U}{\partial W_t^l} \Phi_{t_0, t_0} e^U dW_t^l \\
& = \left[A(t) - \sum_{l=1}^m \frac{1}{2} (C^l(t))^2 - \sum_{l=1}^m \frac{1}{2} (C^l(t))^2 \right] \Phi_{t, t_0} dt \\
& + \sum_{l=1}^m C^l(t) \Phi_{t, t_0} dW_t^l \\
& = A(t) \Phi_{t, t_0} dt + \sum_{l=1}^m C^l(t) \Phi_{t, t_0} dW_t^l \tag{137}
\end{aligned}$$

The last line implies that (135) is the solution of (131).

□

B Programs

Program

```
PRO modelconstant,AH,BH,CH,AH2,N,dt,f,pi,sigma,rho,xgrens,ygrens,zgrens
      ,aantal,cijfer
NH = fltarr(N+1)
NNH = fltarr(N+1)
NNNH = fltarr(N+1)
NH2 = fltarr(N+1)
NNH2 = fltarr(N+1)
deltaNH2 = fltarr(N+1)
R = fltarr(N+1,aantal,aantal)
P = fltarr(N+1,aantal)
Q = fltarr(N+1,aantal)
X = fltarr(N+1,aantal)
Y = fltarr(N+1,aantal)
Z = fltarr(N+1,aantal)
for k=0,N do begin
  print,k
  deltaNH2[k]=0
  NH[k]=0
  NNH[k]=0
  NNNH[k]=0
  NNH2[k] = 0
  for i=0,(aantal-1) do begin
    if k eq 0 then begin
      X[k,i]=2*xgrens*randomn(seed,1,/UNIFORM)
      Y[k,i]=2*ygrens*randomn(seed,1,/UNIFORM)
      Z[k,i]=2*zgrens*randomn(seed,1,/UNIFORM)
      if (Z[k,i]-pi)^2 le sigma then begin
        P[k,i]= 1
      endif
      if (Z[k,i]-pi)^2 ge sigma then begin
        P[k,i]= 0
      endif
      for j=0,(aantal-1) do begin
        if (((x[k,i]-x[k,j])mod xgrens)^2+((y[k,i]-y[k,j])mod
          ygrens)^2+((Z[k,i]-Z[k,j]) mod zgrens)^2) le rho then
          begin R[k,i,j]= 1
        endif
        if (((x[k,i]-x[k,j])mod xgrens)^2+((y[k,i]-y[k,j])mod
          ygrens)^2+((Z[k,i]-Z[k,j]) mod zgrens)^2) ge rho then
          begin R[k,i,j]= 0
        endif
      endfor
      Q[0,i]=0
      NNH[0] = NNH[0]+P(0,i)
      deltaNH2[0]=0
    endif
    if k ge 1 then begin
      Q[k,i]=0
      X[k,i]=((X[k-1,i]+f*sqrt(dt)*randomn(seed,1,/NORMAL)+2*
        *xgrens*randomn(seed,1,/UNIFORM)*(Q[k-1,i]-1)) mod
```

```

(2*xgrens)+2*xgrens) mod(2*xgrens)
Y[k,i]=((Y[k-1,i]+f*sqrt(dt)*randomn(seed,1,NORMAL)+2*
*ygrens*randomn(seed,1,UNIFORM)*(Q[k-1,i]-1)) mod
(2*ygrens)+2*ygrens) mod(2*ygrens)
Z[k,i]=((Z[k-1,i]+f*sqrt(dt)*randomn(seed,1,NORMAL)+2*
*zgrens*randomn(seed,1,UNIFORM)*(Q[k-1,i]-1)) mod
(2*zgrens)+2*zgrens) mod(2*zgrens)
if (Z[k,i]-pi)^2 le sigma then begin
  P[k,i]= 1
endif
if (Z[k,i]-pi)^2 ge sigma then begin
  P[k,i]= 0
endif
if Q[k-1,i] eq 1 then begin
  P[k-1,i]=0
endif
for m=0,(aantal-1) do begin
  if (((x[k,i]-x[k,m])mod xgrens)^2+((y[k,i]-y[k,m])mod
  ygrens)^2+((Z[k,i]-Z[k,m]) mod zgrens)^2) le rho then
  begin R[k,i,m]= 1
  endif
  if (((x[k,i]-x[k,m])mod xgrens)^2+((y[k,i]-y[k,m])mod
  ygrens)^2+((Z[k,i]-Z[k,m]) mod zgrens)^2) ge rho then
  begin R[k,i,m]= 0
  endif
endifor
for l =0,(aantal-1) do begin
  Q[k,i] = Q[k,i]+P[k,i]*P[k-1,i]*P[k,l]*P[k-1,l]*R[k,i,l]
endifor
if Q[k,i] ge 1 then begin
  Q[k,i]=1
endif
NNH[k]=NNH[k]+(P[k,i]*(1-P[k-1,i])-P[k-1,i]*(1-P[k,i]))
NNNH[k]=NNNH[k]+Q[k,i]/2
endif
endifor
if k eq 0 then begin
  NH[k]=NH[k]+NNH[k]
  NH2[k]=0
endif
if k ge 1 then begin
  NH[k] = NH[k-1]+ AH+BH*NNH[k]-2*CH*NNNH[k]
  NH2[k] = NH2[k-1]+AH2+CH*floor(NNNH[k])
  deltaNH2[k]=NH2[k]-NH2[k-1]
endif
endifor
set_plot,'ps'
device,filename = 'Model1_'+string(AH,FORMAT = '(3IO)')+ '_'+
+string(BH,FORMAT = '(3IO)')+ '_'+string(CH,FORMAT = '(3IO)')+
+ '_'+string(AH2,FORMAT = '(3IO)')+ '_'+string(N,FORMAT = '(3IO)')+ '_'+
+string(dt,FORMAT = '(3IO)')+ '_'+string(f,FORMAT = '(3IO)')+ '_'+
+string(pi,FORMAT = '(3IO)')+ '_'+string(sigma,FORMAT = '(3IO)')+ '_'+
+string(rho,FORMAT = '(3IO)')+ '_'+string(xgrens,FORMAT = '(3IO)')+ '_'+
+string(ygrens,FORMAT = '(3IO)')+ '_'+string(zgrens,FORMAT = '(3IO)')+

```

```

+'_'+string(aantal,FORMAT = '(3IO)')+'+'+
+string(cijfer,FORMAT = '(3IO)')+'.ps'
plot,findgen(N+1),NH2,$
  xtitle = 'tijd in rekenronden',ytitle = 'Aantal H- of H_2-moleculen op
  oppervlak, N_{\text{H}}, N_{\text{H}}_2',$
  title = 'Modell_'+string(AH,FORMAT = '(3IO)')+'+'+
+string(BH,FORMAT = '(3IO)')+'+'+string(CH,FORMAT = '(3IO)')+
+'_'+string(AH2,FORMAT = '(3IO)')+'+'+string(N,FORMAT = '(3IO)')+'+'+
+string(dt,FORMAT = '(3IO)')+'+'+string(f,FORMAT = '(3IO)')+'+'+
+string(pi,FORMAT = '(3IO)')+'+'+string(sigma,FORMAT = '(3IO)')+'+'+
+string(rho,FORMAT = '(3IO)')+'+'+string(xgrens,FORMAT = '(3IO)')+
+'_'+string(ygrens,FORMAT = '(3IO)')+'+'+string(zgrens,FORMAT = '(3IO)')+
+'_'+string(aantal,FORMAT = '(3IO)')+'+'+string(cijfer,FORMAT = '(3IO)'),
  ,YRANGE=[0,aantal],Line = 0
oplot,findgen(N+1),NH,Line = 1
oplot,findgen(N+1),deltaNH2,Line = 2
device,/close
set_plot, 'x'
o = fltarr(N+1)
u = fltarr(N+1)
for t=0,N do begin
  o[t] = X[t,1]
  u[t] = Y[t,1]
endfor
set_plot,'ps'
device,filename = 'Modell_positie.ps'
plot,(0*findgen(N+1)),(0*findgen(N+1)),$
  xtitle = 'xpositie',ytitle = 'ypositie',$
  title = 'random walks van deeltjes',Line =0,Psym = 0,XRANGE=[0,2*xgrens],
  ,YRANGE=[0,2*ygrens]
oplot,o,u, Line = 1
device,/close
set_plot, 'x'
END

```

C References

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