# Deterministic and Stochastic Optimal Control for Batch Cooling Crystallization

Tushar Gupta

## Abstract

Minimization of operation costs and the enhancement in product quality have been major concerns for all industrial processes. The field under study here is batch crystalllization which is affected heavily by the uncertainities in measurements and other errors. This work analyses various optimization approaches for the batch crystallization process that are robust to model error. All of the methods involve maximising an objective function by manipulating the cooling profile. At first, the Deterministic approach uses experimental kinetic parameters, which is then extended to Stochastic optimization to incorporate uncertainities in them. Lastly, a novel approach named Polynomial Chaos Expansions is implemented which has been applied successfully to other domains for Nonlinear Model Predictive Control but was not explored in detail in the field of batch cooled crystalllization. It successfuly includes probability distributions for the parameters into the model to provide a more robust optimization srategy.

*Keywords:* Stochastic Optimal Control, Polynomial Chaos Expansions, Robust Optimization, Batch Crystallization, Predictive Control, Optimum Temperature Profile

## 1. Introduction

Numerous industries today, such as pharmaceutical, chemical, photographic etc. employ the batch crystallization process for the preparation of crystalline products with high degree of purity. A common goal of each crystallization process is to obtain a narrower Particle size distribution (PSD) of the desired product. The PSD has a strong influence on the downstream processing and, hence, reproducible PSD in each operation is of prime importance. Thus, finding an effective control strategy to obtain the resulting crystals with a desired Crystal Size Distribution becomes significant in order for improving the performance of both the batch crystallization process and the subsequent processes which depend on it.

Crystallization is the (natural or artificial) process where the atoms or molecules are highly organized into a solid structure known as a crystal. Some of the ways which crystals form are through precipitating from a solution, melt or more rarely deposited directly from a gas. In order for crystallization to take place a solution must be "*super-saturated*". **Supersaturation**($\Delta C$) is a condition in which the solute concentration in the solution is higher than the solubility. It acts as the driving force for the crystallization process and affects the final quantity of product formed. It is mathematically expressed as :

$$\Delta C = C - C_s \tag{1}$$

where $C_s$ is the concentration of the solute in the saturated solution. In the following work, the method in focus is cooling crystallization in which superstauration magnitude is determined by the cooling rate. Thus, determination of an optimal cooling rate or a temperature trajectory becomes the objective of the currrent study.

This work formulates and analyses various control strategies for a cooling crystallization process represented through the population balance equation. **Deterministic Optimal Control** aims at finding the an optimum temperature profile to maximise an objective function selected to achieve a desired volume of the product. Herein, the experimental kinetic parameters are employed to simulate a batch crystalllization process. **Stochastic Optimal Control** undertakes the task of quantifying the uncertainites which creep in due to experimentation. It aims to achive a maximum expected value for the desired product, simultaneously incorporating randomness in the process parameters into the model. Namely, two methods **Ito Process** and a novel approach **Polynomial Chaos Expansions** are employed for this purpose.

Most of the reported works in the this field deal with the determination of optimal temperature or supersaturation trajectory for the batch crystallizer. The concept of programmed cooling in batch crystallizers was first discussed by Mullin and Nỳvlt (1971). Later, Jones (1974) presented a mathematical theory based on moment transformations of population balance equations. He used the continuous maximum principle to predict optimal cooling curves. Rawlings et al. (1992) discussed issues in crystal size measurement using laser light scattering experiments and optimal control problem formulation. Miller and Rawlings (1994) discussed the uncertain bounds on model parameter estimates for a batch crystallization system. Most importantly optimal temperature prediction for batch crystallization has also been done by Hu et al. (2005), Shi et al. (2006), Paengjuntuek et al. (2008) and Corriou and Rohani (2008), the data and knowledge from which have been used in further work in this project.

Stochastic modeling of particulate processes and parameter estimation using the experimentally measured particle sizes has attracted many researchers. Grosso et al. (2011) presented a stochastic approach for modeling PSD and comparative assessments of different models. Ma et al. (1999) presented a worse-case performance analysis of optimal control trajectories by considering features such as the computational effort, parametric uncertainty and control implementation inaccuracies. Monte Carlo simulations have also been used to propogate uncertainities but often present the problem of high computational demand, for which this work proposes Polynomial Chaos Expansions(PCEs) as an alternative. The computational advantages of PCEs for robust control and optimization has been shown by Nagy and Braatz (2007), Kim and Braatz (2012) and Kumar and Budman (2014).

The focus of the current research activity is to incorporate parametric uncertainties in the mathematical formulations of batch crystallization process for building a robust model. In the deterministic approach, kinetic parameters from the experimental data have been used to model the system. Next, stochastic Ito processes are used to assimilate the errors in the experimental data. Finally, PCE are demostrated as an effective method for non-linear optimization in batch reactors. A case study of an unseeded crystallization process is also included to authenticate the methodology.

## 2. Materials and methods

This section introduces the underlying concepts needed to build a computational model of a crystallization process which involves regulating the population of particles, also termed as a particulate process. The population is described by the density of a suitable extensive variable, usually the **number of particles**, but sometimes by other variables such as the mass or volume of particles. The usual transport equations expressing conservation laws for material systems apply to the behavior of single particles. Particulate processes are characterized by properties such as particle shape, size, surface area, mass, and product purity.

A population balance formulation describes the process of crystal size distribution with time most effectively. Thus, modeling of a batch crystallizer involves the use of population balances to model the crystal size prediction and the mass balance on the system can be modeled as a simple differential equation having concentration as the state variable. The population balance can be expressed as eq :

$$\frac{\partial n(r,t)}{\partial t} + \frac{\partial G(r,t)n(r,t)}{\partial r} = B \tag{2}$$

where **n** is the number density distribution, **t** is the time, **r** represents the characteristic dimension for size measurements, **G** is the crystal growth rate, and **B** is the nucleation rate. Both growth and nucleation processes describe crystallization kinetics, and their expression may vary, depending on the system under consideration.

In this work, the system under consideration is potassium sulfate, which has been studied earlier for its kinetics by Hu et al. (2005), Shi et al. (2006) and Paengjuntuek et al. (2008). The equations expressing the kinetics and values for the kinetic parameters have been derived form these literary works.

Nucleation kinetics are defined by :

$$B(t) = k_b \exp\left(-E_b/RT\right)\left(\frac{C - C_s(T)}{C_s(T)}\right)^b \mu_3 \tag{3}$$

Growth Kinetics are given by:

$$G(t) = k_g \exp\left(-E_g/RT\right)\left(\frac{C - C_s(T)}{C_s(T)}\right)^g \tag{4}$$

where $k_b$ and $k_g$ are constants of the system, $E_b$ and $E_g$ are activation energies, and b and g are exponents of nucleation and growth, respectively. The values for these parameters for the given system have been mentioned in Table 1. The following equations are used to evaluate the saturation($C_s$) and metastable($C_m$) concentrations corresponding to the solution temperature T (expressed in units of °C) (Shi et al. (2006)).

$$C_s(T) = 6.29 \times 10^{-2} + 2.46 \times 10^{-3}T - 7.14 \times 10^{-6}T^2 \tag{5}$$

$$C_m(T) = 7.76 \times 10^{-2} + 2.46 \times 10^{-3}T - 8.1 \times 10^{-6}T^2 \tag{6}$$

The mass balance, in terms of concentration of the solute in the solution, is expressed as :

$$\frac{dC}{dt} = -3\rho k_v G(t)\mu_2(t) \tag{7}$$

where $\rho$ is the density of the crystals, $k_v$ the volumetric shape factor, and $\mu_2$ is the second moment of particle size distribution (PSD). Since $n(r,t)$ represents the population density of the crystals, the i-th moment of the particle size distribution(PSD) is given by :

$$\mu_i = \int_0^\infty r^i n(r,t)dr \tag{8}$$

The above equations along with the Population Balance Equation(PBE) (2) represent a complete model of a seeded batch crystallizer. Population balance equations are multidimensional, which poses a problem with their implementation in complex control functions, hence use of a model order reduction becomes imperative.

For simplification, we reduce the population balance equations into **Moment balance equations** which has been estabilished as an efficient method by Yenkie and Diwekar (2012). This is done by multiplying the equation (2) with $r^i$ on both sides to generate the expression given by equation (8). Converting the model into Ordinary differential equations proves to be advantageous, since it is difficult and time-consuming to formulate an optimization problem involving PBEs. Thus, the moment method leads to a reduced-order model given by Equations (11) to (14)

Separate moment equations are used for the seed and nuclei classes of crystals, and they are defined as :

$$\mu_i^n = \int_0^{r_g} r^i n(r,t)dr \tag{9}$$

$$\mu_i^s = \int_{r_g}^\infty r^i n(r,t)dr \tag{10}$$

**n** in the superscript represents the nucleated crystal whereas **s** stands for the seeded crystal, $r_g$ gives the critical radius separating the two. The resultatnt moment equations for nucleated and seeded crystals are as follows (Yenkie and Diwekar (2012)) :

1. Nucleated crystals

$$\frac{d\mu_0^n}{dt} = B(t) \tag{11}$$

$$\frac{d\mu_i^n}{dt} = iG(t)u_{i-1}^n(t) \quad i = 1, 2, 3 \tag{12}$$

2. Seeded crystals

$$\mu_0^s = constant \tag{13}$$

$$\frac{d\mu_i^s}{dt} = iG(t)u_{i-1}^n(t) \quad i = 1, 2, 3 \tag{14}$$

The total moment is obtained as the summation $\mu_i^t = \mu_i^n + \mu_i^s$. Here, $\mu_0^s$ represents the amount of seeded crystals and hence remains constant. Also, fourth-order moments and higher do not affect third-order moments and lower, implying that only the first four moments and concentration can adequately represent the crystallization dynamics (Shi et al. (2006)).

The crystallization model defined above has been used to compare the performance of different types of optimization techniques, both in the deterministic and stochastic domain, which is explained in detail in the susequent sections.

Table 1. Experimental values of Kinetic Parameters

| Parameters | Experimental Values |
|:---:|:---:|
| Growth Kinetics | |
| $k_g$ | $1.44 \times 10^8 \mu m s^{-1}$ |
| $E_g/R$ | $4859 K$ |
| $g$ | $1.5$ |
| Nucleation Kinetics | |
| $k_b$ | $285(s \mu m^3)^{-1}$ |
| $E_b/R$ | $7517 K$ |
| $b$ | $1.45$ |

## 3. Deterministic Optimal Control

### 3.1. Case Study : Seeded batch crystallization

Optimal control involves the evaluation of time-dependent operating profiles, in terms of the control variable to optimize the process performance. In the crystallization domain, temperature becomes the control variable while the product yield is used to evaluate the performance of the model. The Optimization problem here is solved by using the method of Maximum Principle as discussed extensively by Diwekar (2008). This method stands out in compared to other techniques such as dynamic programming as it involves the use of first order ODEs while the later utilises partial differential equations. Another advantage of maximum principle is its ability to adapt to stochastic calculus which is explained in the next section.

In a seeded crystallization process it is essential to keep the nucleation phenomena to minimum as in the early stages of growth, nucleated crystals might compete with the seeded ones for growth. This ensures uniformity in the shape and size of the final product. It is achieved by incorporating the volume of nucleated in the **objective fuction**. Third moment($\mu_3$) represents volume in a crystallization model as evident from Equation(8) and is used as follows :

$$\max_{T(t)}\{\mu_3^s(t_f) - \mu_3^n(t_f)\} \tag{15}$$

The active constraints for the process are given by :

$$C_s \leqslant C \leqslant C_m \tag{16}$$

$C_m$ is the metastable concentration described by Equation(6). The state variables $y_i$ for the process are now representes as :

$$y_i = \begin{bmatrix} C & \mu_0^s & \mu_1^s & \mu_2^s & \mu_3^s & \mu_0^n & \mu_1^n & \mu_2^n & \mu_3^n \end{bmatrix} \tag{17}$$

Using the above notations the state equations can be realized as (Yenkie and Diwekar (2012)) :

$$\frac{dy_1}{dt} = -3\rho k_v G(t)(y_4 + y_8) \tag{18}$$

$$\frac{dy_2}{dt} = 0 \tag{19}$$

$$\frac{dy_3}{dt} = G(t)y_2 \tag{20}$$

$$\frac{dy_4}{dt} = 2G(t)y_3 \tag{21}$$

$$\frac{dy_5}{dt} = 3G(t)y_4 \tag{22}$$

$$\frac{dy_6}{dt} = B(t) \tag{23}$$

$$\frac{dy_7}{dt} = G(t)y_6 \tag{24}$$

$$\frac{dy_8}{dt} = 2G(t)y_7 \tag{25}$$

$$\frac{dy_9}{dt} = 3G(t)y_8 \tag{26}$$

$$\tag{27}$$

Thus, the complete model involving the moment equations consists of nine state equations.

### 3.2. Solution technique

The algorithm of Steepest Ascent utilizes the Maximum Principle using the Hamiltonian to move towards the optimum value of temperature and maximise the objective function. To formulate the equations an adjoint varible ($z_i$) is defined corresponding to each state variable ($y_i$) The adjoint variable staisfy the relations given by eq 31. Using the state and the adjoint equations, a two-point boundary-value-problem is constructed. Here, the intial values for the states and the final conditions for the adjoint variables are known beforehand. The Hamiltonian can now be defined by eq 28.

$$H = \sum_{i=1}^{9} z_i f(y_i, t, T) \tag{28}$$

The complete model with the objective function is given by Equations (29) to (31):

$$max_{T(t)}\{y_5(t_f) - y_9(t_f)\} \tag{29}$$

$$\frac{dy_i}{dt} = f(y_i, t, T) \tag{30}$$

$$\frac{dz_i}{dt} = \sum_{j=1}^{9} z_j \frac{\partial f(y_i, t, T)}{\partial y_i} = f(y_i, z_i, t, T) \tag{31}$$

with the initial and final conditions:

$$t_0 = 0 \quad and \quad t_f = 1800s \quad (batch \quad time)$$
$$y_i(t_0) = \begin{bmatrix} 0.1743 & 66.66 & 1.83 \times 10^4 & 5.05 \times 10^6 & 1.93 \times 10^9 & 0.867 & 0 & 0 & 0 \end{bmatrix}$$
$$z_i(t_f) = [0 \quad 0 \quad 0 \quad 0 \quad 1 \quad 0 \quad 0 \quad 0 \quad -1]$$

The steps followed to solve the optimal control problem have been discussed in detail below.

1. An initial temperature $T(t) = 323K$ is assumed for the entire time horizon.

2. The differential equations for state variables are integrated in the forward direction using the given initial conditions.

3. The values of the adjoint variables are computed by backward integration of the adjoint equations given by eqs. 31.

4. For evaluation of the Hamiltonian derivative, an analytical method proposed by Benavides and Diwekar (2012), is used in which an additional variable corresponding to each of the state and adjoint variable is introduced. The variable $\theta_i$ corresponds to each of the state variable $y_i$ and the variable $\phi_i$ corresponds to each of the adjoint variable $z_i$, which is given by eq(32).

$$\theta_i = \frac{dy_i}{dT} \quad and \quad \phi_i = \frac{dz_i}{dT} \tag{32}$$

5. The Hamiltonian derivative is now calculated at each time step by the eq(33)

$$\frac{dH}{dT} = \sum_{i=1}^{9} \left(\frac{dH}{dy_i}\right)\left(\frac{dy_i}{dT}\right) + \sum_{i=1}^{9} \left(\frac{dH}{dz_i}\right)\left(\frac{dz_i}{dT}\right) \tag{33}$$

6. The computed value of the derivative is checked against the convergence criterion ($\frac{dH}{dT}$ < tolerance). If it is not satisfied, the temperature $T(t)$ is updated using eq(34). This ensures that the optimal control variable $T(t)$ is obtained using the extremum of hamiltonian.

$$T^{new}(t) = T^{old}(t) + M\left(\frac{dH}{dT}\right) \tag{34}$$

7. The concentration is evaluated at that time step and compared with first with the saturation concentration ($C_s$) and then the metastable concentration($C_m$) to validate the active constraints. If it found to be lesser than saturation value or greater than the metastable value, eqs (5) and (6) are used to compute the new temperature respectively.

8. Iterations of above steps are repeated until the convergence criteria is achieved.

### 3.3. Results

The integration of differential equations was performed in python using the odeint routine from the scipy open source package. The resultant optimal temperature profile is shown in Figure (1). The system attains a constant value of $300K$ at $\sim 1700s$. The decreasing temperature profile is indicative of the cooling crystallization. Also, the objective function can be observed to reach a maximum value in the Figure(2). The concentration profile of solute in the system is given by the Figure(3).
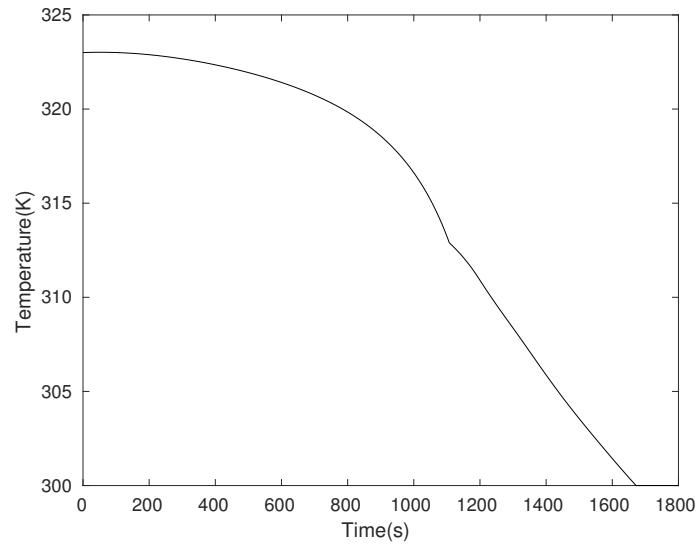
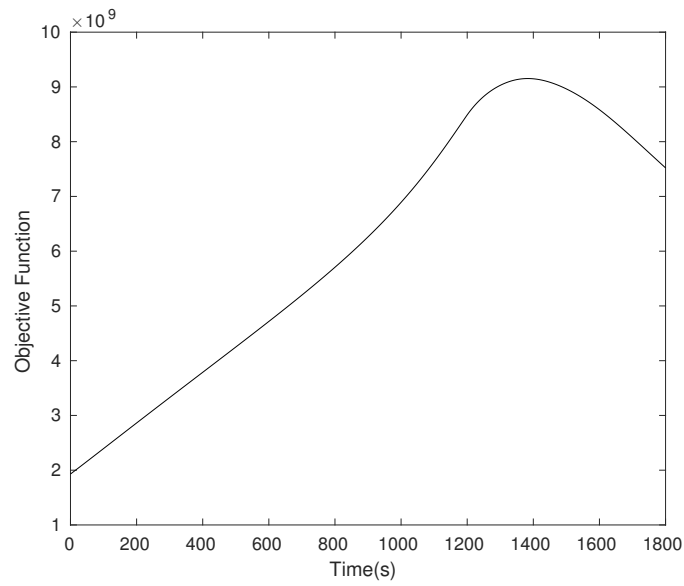Figure 1. The cooling profile for the controlled variable T(t) obtained at the final iteration



Figure 2. Objective Function $(\mu_3^s(t) - \mu_3^n(t))$

## 4. Optimal Control using Uncertainity Quantification

The kinetic parameters used in the Section(3) are empirical constants which are obtained through experimentation and hence, are a source of errors into the model. The exact values of the parameters are unknown and thus are termed as uncertainties which go on to produce sub-optimal results when used in real-world applications. In the
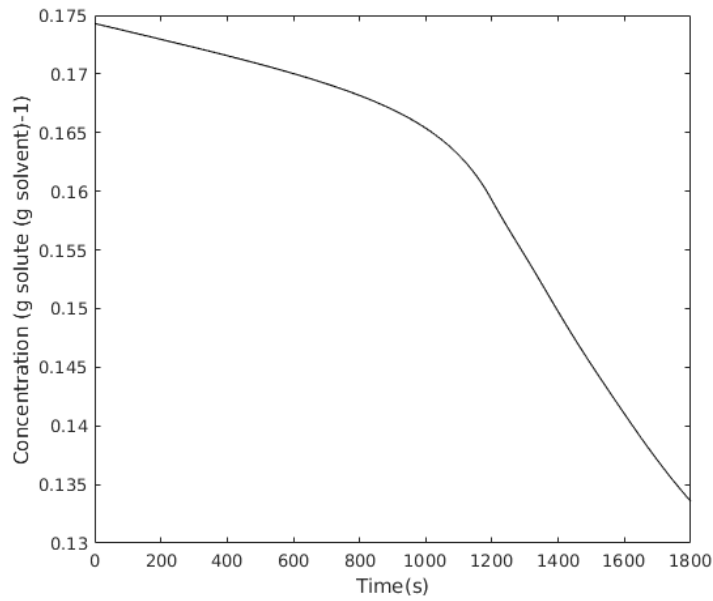
Figure 3. The Concentration profile as obtained.

next section, we convert the deterministic problem into a stochastic one, wherein the kinetic constants are treated as random variables to include variation in there values into the final output produced by the model. Thus, two methods are analysed to address the given problem.

### 4.1. Stochastic Optimal Control using Ito Processes

Several previous works have shown that the dynamic uncertainties present in batch reactors (Benavides and Diwekar (2012)) and batch distillations (Diwekar (2008)), can be represented using stochastic processes known as Ito processes. We characterize the time-dependent uncertainties in the state variables using Ito processes known as Brownian motion with drift (Diwekar (2008); Eugene and Moshe (1965)). The advantage lies in the ability to integrate the equations through the principles of stochastic calculus and the use of stochastic maximum principle to solve for the optimal temperature profile. A simple Ito process can be written as eq (35)

$$dy = a(y, t)dt + b(y, t)dz \tag{35}$$

where $dz$ is the increment of the Wiener process equal to $\varepsilon_t(\Delta t)^{1/2}$, and a(y,t) and b(y,t) are known functions. The random value $\varepsilon_t$ has a unit normal distribution with zero mean and a standard deviation of 1. To estimate the values of the functions a and b, a generalized method presented by Diwekar (2008) has been used.

In this work, equation(35) is used to modify the deterministic state (Equations (18) to (26)) to incorporate the

uncertainties into the moment equations as follows :

$$dy_1 = (-3\rho k_v G(t)(y_4 + y8))\,\Delta t + g_1\varepsilon_1\,\sqrt{\Delta t} \tag{36}$$

$$dy_2 = 0 \tag{37}$$

$$dy_3 = (G(t)y_2)\Delta t + g_3\varepsilon_3\,\sqrt{\Delta t} \tag{38}$$

$$dy_4 = (2G(t)y_3)\Delta t + g_4\varepsilon_4\,\sqrt{\Delta t} \tag{39}$$

$$dy_5 = (3G(t)y_4)\Delta t + g_5\varepsilon_5\,\sqrt{\Delta t} \tag{40}$$

$$dy_6 = (B(t))\Delta t + g_6\varepsilon_6\,\sqrt{\Delta t} \tag{41}$$

$$dy_7 = (G(t)y_6)\Delta t + g_7\varepsilon_7\,\sqrt{\Delta t} \tag{42}$$

$$dy_8 = (2G(t)y_7)\Delta t + g_8\varepsilon_8\,\sqrt{\Delta t} \tag{43}$$

$$dy_9 = (3G(t)y_8)\Delta t + g_9\varepsilon_9\,\sqrt{\Delta t} \tag{44}$$

$a(y, t)$ in each equation is replaced by the corresponding deterministic function for the state variable. Here, the $g_i$ values represent the variance in the variable for which they are associated. They are calculated by recording the variance of the differences $(y_i^t - y_i^{t-1})$, which is divided by the time interval $\Delta t$, and then the square root of this value is taken.

The stochastic system defined by the Equations (36) to (44) treats the kinetic parameters as random variables for which the variations are propagated through the coefficients $g_i$ into the final output of the model. The range of values exhibited by the kinetic constants can be seen in the Table (2) (Hu et al. (2005), Shi et al. (2006) and Paengjuntuek et al. (2008)). We use a Gaussian probabilistic distribution (Yenkie and Diwekar (2012)) to incorporate the variations into the model. Consequently, the objective function is also modified in 45 for its evaluation in the stochastic domain.

$$\max_T L = \mathbf{E}\left[\mu_3^s(t_f) - \mu_3^n(t_f)\right] \tag{45}$$

Here, $\mathbf{E}$ is the expected value of the variable. The new objective function maximizes the expected value of mass of the seeded crystals for an optimal temperature profile in presence of errors or uncertainties in values of concentration or the moments, thus making it more suited to real world scenarios. The **Active Constraints** and **Initial Conditions** remain the same as mentioned in Section (3).

Table 2. Uncertainties in Kinetic Parameters

| Parameters | Experimental Values | Range of Values |
|---|---|---|
| Growth Kinetics | | |
| $k_g$ | $1.44 \times 10^8 \mu m s^{-1}$ | $1.368 - 1.512 \times 10^8$ |
| $E_g/R$ | $4859K$ | $4606.15 - 5101.95$ |
| $g$ | $1.5$ | $1.425 - 1.575$ |
| Nucleation Kinetics | | |
| $k_b$ | $285(s\mu m^3)^{-1}$ | $270.75 - 299.25$ |
| $E_b/R$ | $7517K$ | $7141.15 - 7892.85$ |
| $b$ | $1.45$ | $1.3775 - 1.5225$ |

### 4.1.1. Solution Technique

The optimization problem for the given system is solved by extending the maximum principle to the Stochastic Maximum Principle (Rico-Ramirez and Diwekar (2004)), through the Steepest Ascent Hamiltonian method similar to Section (3.2). The Hamiltonian for this section is modified to incorporate the uncertainties as (Yenkie and Diwekar (2012)):

$$H = \sum_{i=1}^{9}\left(z_i f_i + \omega_i \frac{g_{y_i}^2}{2}\right) \tag{46}$$

Here, $f_i$ are the deterministic functions used on L.H.S for the . $\omega_i$ is an additional adjoint variable defined to calculate the Hamiltonian. The **Algorithm** for the method remains same as mentioned in Section (4.1.1) with minor changes.

1. Steps (1-4) are repeated.
2. The variable i corresponds to each of the state variable yi and the variable i corresponds to each of the adjoint variable zi , i corresponding to each i respectively.
3. The variable $\theta_i$ corresponds to each of the state variable $y_i$ and the variable $\phi_i$ corresponds to each of the adjoint variable $z_i$, $\psi_i$ for each $\omega_i$ respectively.
4. The Hamiltonian derivative is now calculated at each time step as :

$$\theta = \frac{dy_i}{dT} \quad \phi_i = \frac{dz_i}{dT} \quad \psi = \frac{d\omega_i}{dT} \tag{47}$$

$$\frac{dH}{dT} = \sum_{i=1}^{9}\left(\frac{dH}{dy_i}\right)\left(\frac{dy_i}{dT}\right) + \sum_{i=1}^{9}\left(\frac{dH}{dz_i}\right)\left(\frac{dz_i}{dT}\right) + \sum_{i=1}^{9}\left(\frac{dH}{dw_i}\right)\left(\frac{dw_i}{dT}\right) \tag{48}$$

5. The convergence criteria and the constraints remain same as the above referenced method.

### 4.1.2. Results

The stochastic differential equations are integrated using stochastic calculus through **SDE Tools** Library available in **Matlab**.A strong Taylor approximation from the **Euler Maruyama** scheme has been used to integrate the equations which has an order of convergence of 0.5. Table(3) contains the values for $g_i$ that were used as the coefficients for uncertainties for the state variables. In this case, the system reaches to a maximum value of the objective function at $\sim 800s$ as seen in Figure(4). The obtained temperature profile is decreased to $309K$ at the end of batch time in Figure(5).

Table 3. State Variable Uncertainty CoefficientsYenkie and Diwekar (2012)

| Parameters | Values |
|---|---|
| $g_1$ | $2.659 \times 10^{-5}$ |
| $g_2$ | $0$ |
| $g_3$ | $25.882$ |
| $g_4$ | $1.517 \times 10^{4}$ |
| $g_5$ | $6.57 \times 10^{6}$ |
| $g_6$ | $0.5486$ |
| $g_7$ | $25.9$ |
| $g_8$ | $1382.34$ |
| $g_9$ | $8.753 \times 10^{4}$ |

### 4.2. Stochastic Optimal Control using Polynomial Chaos Expansion(PCE)

The generalized polynomial chaos (PC) framework has been proven as a computationally efficient alternative for uncertainty propagation through a nonlinear system, as opposed to the Monte-Carlo simulations. In the following work, we use PCE to fit the crystallization model using orthogonal polynomials and compare the performance with the other methods in this domain.

### 4.2.1. Mathemetical Background

A Polynomial Chaos Expansion (PCE) describes a random process as a spectral expansion of random variables($\theta_i$), using orthogonal basis functions, $\Phi_i$ (Ghanem and Spanos (1990), Ghanem and Spanos (1997)). For example, any second-order (finite variance) random process $y^d$, can be described using a PCE as follows:

$$y^d = a_0^d\phi_0 + \sum_{i_1=1}^{\infty} a_{i_1}^d \phi_1(\theta_{i_{i1}}) + \sum_{i_1=1}^{\infty}\sum_{i_2=1}^{i_1} a_{i_1 i_2}^d \phi_2(\theta_{i_1}, \theta_{i_2}) \tag{49}$$
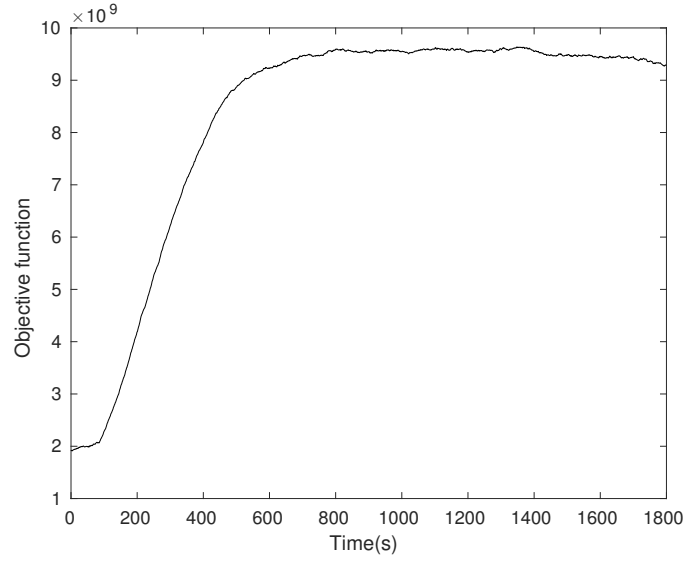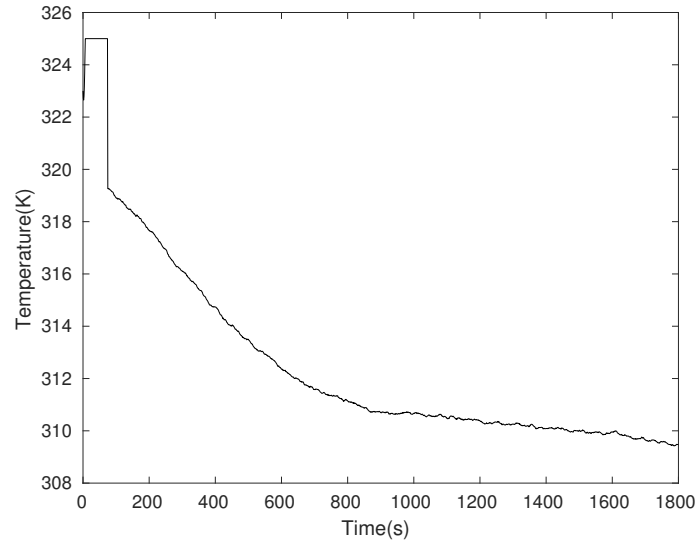
Figure 4. Objective Function ($\mathbf{E}\left(\mu_3^s(t) - \mu_3^n(t)\right)$)



Figure 5. The optimum cooling profile for the system

where $a_{i_1}^d$ are deterministic coefficients for each term in the expansion. The number of independent sources of random variables $(\theta_{i_1}, \theta_{i_2})$, generally defines the dimensionality, $n_0$. For practical application these expansions can be truncated to a finite number of terms. Then the maximum polynomial order for the basis function, q needs to be defined. The number of terms now become $P_{PCE} = \frac{(n_0+q)!}{n_0!q!} - 1$. Using these notations, a reduced PCE expansion can be represented as follows:

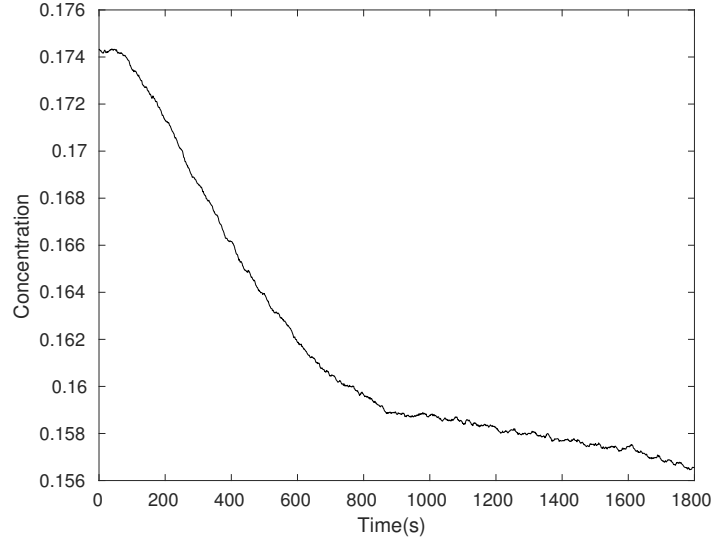$$y^d \approx \sum_{i=1}^{P_{PCE}} a_i^d \phi_\theta \qquad (50)$$

11

Figure 6. Concentration Profile

The orthogonality property of the basis functions($\phi_i$) is used for the calculation of the coefficients when propagating uncertainty from the input random variables($\theta_{i_1}, \theta_{i_2}$), to the output random variables ($y^d$). The choice of the basis functions $\phi_i$ depends on the type of stochastic distribution to be represented, i.e. normal or uniform. In our case the parameters follow a Gaussian distributionYenkie and Diwekar (2012), which uses Hermite Polynomials to describe the probability distribution in the least number of terms.

Thus, given a process model with uncertain output, $y = X(x, \lambda)$, where $x$ is the uncertain input and $\lambda$ is the uncertain parameter, the aim is to quantify uncertainty in $y(\theta)$ from $x(\theta), \lambda(\theta)$ using the process model. Then the first step is to construct PCEs of $x(\theta)$, and $\lambda(\theta)$, by determining their PCE coefficients $x_i$ and $\lambda_i$.

$$x(\theta) = \sum_{i=1}^{P_{PCE}} x_i \phi(\theta) \lambda(\theta) \qquad\qquad = \sum_{i=1}^{P_{PCE}} \lambda_i \phi(\theta) \qquad (51)$$

$$x_i = \frac{\int x \phi_i(\theta) g(\theta) d\theta}{\left\langle \phi_i^2 \right\rangle} \qquad\qquad \lambda_i = \frac{\int \lambda \phi_i(\theta) g(\theta) d\theta}{\left\langle \phi_i^2 \right\rangle} \qquad (52)$$

where $g(\theta)$ is probability distribution function (pdf) of $\theta$. The next step is to develop PCE for $y(\theta)$ from $x(\theta)$, and $\lambda(\theta)$, which can be done by evaluating the inner product of $y(\theta)$ with each basis functions $\phi_i$ to determine the ith- PCE coefficient.

$$y_i = \frac{\langle f(x, \lambda) \phi_i \rangle}{\left\langle \phi_i^2 \right\rangle} \qquad (53)$$

Evaluating the inner product $\langle y \phi_i \rangle$, requires computation of multi-dimensional integrals which can be performed by one of two approaches referred to as **non-intrusive** and **intrusive**.

### 4.2.2. Usage of PCE in Batch Crystallization

Extending the concepts from the previous section, the state varibles($y_i$)(Equations (18) to (26)) act as the uncertain outputs which is caused by uncertainities present in process parameters $\lambda$ ($k_g, E_g, g, k_b, E_b, b$), used to calculate the Growth rate ($G(t) = k_g \exp\left(-E_g/RT\right) \left(\frac{C - C_s(T)}{C_s(T)}\right)^g$) and the Nucleation rate ($B(t) = k_b \exp\left(-E_b/RT\right) \left(\frac{C - C_s(T)}{C_s(T)}\right)^b \mu_3$).

Temperatue($T(t)$) acts as the input variable $x$ in the above system. The PC expansion coefficients can be determined using the probabilistic collocation methods. Using these methods, N samples are drawn from the known distributions of uncertainties and, subsequently, are used to solve the nonlinear process model Equations (29) to (31). The PC expansion coefficients can then be obtained in a least squares sense by minimizing the residuals between the PC expansion and the nonlinear model predictions. The complete algorithm is mentioned below.

**Algorithm**:

1. Following the general representation, $y_i$ can be written as :

$$y_i = f(x(\theta), \lambda_i(\theta))$$

   where x is the input temperature(T), $\lambda_i$'s are process parameters and $\theta$ is the random variable.

2. The process model consists of 6 uncertainities which computationally prohibits the evaluation. Thus, an approximation of $n_0 = 2$ is taken by employing a joint distribution of the parameters.

3. Samples are generated for the model at $N$ points. The sampling technique used is the Gaussian Quadratures along with Hermite Polynomials to represent state variables ($y_i$) into Eq(5.17).

4. For each of the above sample $y_i^j = f(T^j(\theta), \lambda(\theta))$ , the optimization problem is solved using the Steepest Ascent Hamiltonian method discussed in Section(4.1.1).

5. The optimum value of the input temperature $T^j(\theta)$ at these samples is used to construct the PCE's for $T(\theta)$ and $\lambda(\theta)$ as given by Equations(5.18).

6. $y_i^j$'s for each sample are used to evaluate :

$$y_i = \frac{1}{\langle \phi_i^2 \rangle} \frac{1}{N} \sum_{j=1}^{N} y^j \phi_i(\theta) \tag{54}$$

   Here, $\phi_i$ are the coefficients of the orthogonal polynomials being used for PCE estimation.

7. As the above Equation averages over N samples, the resultant $y_i$ maximises the objective function, given by $\mathbf{E}\{y_5 - y_9\}$).

### 4.2.3. Results

All the source scripts for using PCE with the crystallization model were written Python, using the open source library **chaospy**Feinberg and Langtangen (2015). It is a toolbox for performing uncertainity quantification through polynomial chaos expansions and efficient sampling strategies. The base model for performing simulations was derived from Section 3. The range of values exhibited by the uncertain parameters have been mentioned in the Table 2. The results obtained can be observed from section 4.2.3

## 5. Case Study

In the following case study we aim to build a predictive model for batch crystallization of L-Asparagine Mono-hyrdate(LAM) by using the concepts developed in the previous section and at the same time validate the performance of Polynomial Chaos Expansions (PCEs) on an unseeded batch crystallization scenario.

### 5.1. Mathematical Background

The kinetics of crystal formation are modeled using the population balance equations(PBE) in 2, where the nucleation rate expression for LAM crystals is given by **?** :

$$B = k_{j_1} S \exp\left(-k_{j_2} \frac{\ln^3 C_c/C^*}{\ln^2 S}\right) \tag{55}$$

in which $C_c$ represents the molar density of LAM crystals. Here, $k_{j_1}$ and $k_{j_2}$ are empirical parameters. The growth rate is now given by the power-law expression given by Nagy and Braatz (2007) and **?**:
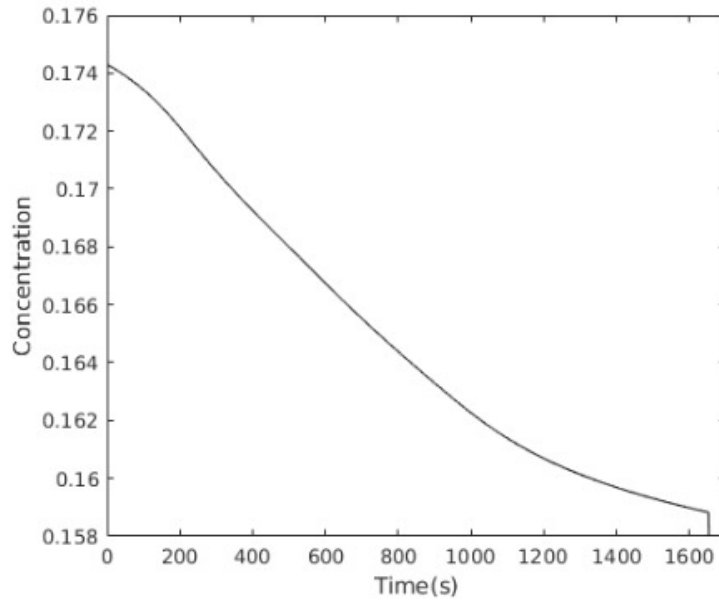
$$G = k_g(S - 1)^g \tag{56}$$

Figure 7. The Concentration profile

The supersaturation ratio, S, is defined as :

$$S = C/C^*$$  (57)

where $C^*$ represents the saturation concentration of LAM crystals. The solubility of these crystals can be expressed as:

$$C^* = 5 \times 10^{-5} T^2 - 0.001T + 0.0236$$  (58)

The values for the set of kinetic parameters $[k_g, g, k_{j_1, k_{j_2}}]$ have been mentioned in the 4 (**?**).

Table 4. Kinetic Parameters

| Parameters | Experimental Values | Range of Values |
|---|---|---|
| Growth Kinetics | | |
| $\ln(k_g)$ | $3.41 \pm 0.28$ | $\mu m min^{-1}$ |
| $g$ | $1.48 \pm 0.04$ | – |
| Nucleation Kinetics | | |
| $\ln(k_{j_1})$ | $24.74 \pm 0.73$ | $No. per m^3 min$ |
| $k_{j_2}$ | $2.7 \times 10^{-2} \pm 3.2 \times 10^{-3}$ | – |

Method of Moments has been used to reduce the PBE to ODE's as stated in Section **??**. The mass balance for LAM crystals also remains the same from there, with the difference being the absence of seeded crystals.

The ODEs for the model are given by :

$$\frac{du_0}{dt} = B$$  (59)

$$\frac{du_j}{dt} = jG\mu_{j-1}$$  (60)

14

for $j = 1, 2, 3, 4$

The determination of the optimal temperature profile for maximizing the weight mean size is a highly studied objective for a crystallization process.Thus,

*Objective Function.* becomes :

$$\max_{T(t)} \phi = \mu_4/\mu_3 \quad at \quad t_f \tag{61}$$

*Constraints.*

$$T_{min} \leqslant T(t) \leqslant T_{max} \tag{62}$$

$$\frac{dT}{dt} \leqslant 0 \tag{63}$$

The state variables can be represented as :

$$y_i = \begin{bmatrix} C & \mu_0 & \mu_1 & \mu_2 & \mu_3 & \mu_4 \end{bmatrix}$$

Here we do not divide the moments in seeded and nucleated ones.

The Hamiltonian method described in the previous sections was employed to solve the optimaization problem along with the uncertainity quantification being done using Polynomial Chaos Expansions. The new state equations, constraints and kinetics as described above are used to define the problem.

### 5.2. Solution Technique : Hamiltonian Steepest Ascent with PCE

Equations(6.5-6.6) take place as the new state equations and the uncertain parameters are mentioned in Table 6.1. The constraint(Eq 6.9)) depicts a cooling profile for the crystallizer. The obejective function here (Eq 6.7) differs from the one used in Section(**??**) so as to calculate the final maximum mean size of the crystals.

Key Differences :

- The batch time for the model was taken to be 240 min($t_f$).

- An initial concentration value of 0.073 $g/L$ was taken to obtain the cooling profile. All the moments were intialised to 0.

- The ODEs were integrated using Python **scipy's odeint** integrator.

*Algorithm.*

1. The process model consists of 4 uncertainities which computationally prohibits the evaluation. Thus, the experiment has been done on $k_g$ and $g$, employing a joint distribution of the parameters.
2. Samples are generated using the distribution using Gaussian Quadrature Scheme.
3. The function is evaluated at each of these samples to evalute the integrals numerically to determine the PCE coefficients.
4. At each sample, optimization of the model is performed using the Determinstic Approach explained in Section(**??**).
5. The convergence criteria and the constraints remain same as the above referenced method.

### 5.3. Results

The value for the concentration profile for the time horizon was obtained as :

The value for the temperature profile was obtained as :

### 5.4. Conclusion

- The final value of the objective function($\mu_4/\mu_3$), ie. the mean crystal size was obtained at : $300\mu m$

- The model performs at par with other cooling policies such as cubic cooling policy($251\mu m$)**?**. This proves the efficacy of P.C.E in the field of batch crystallization.
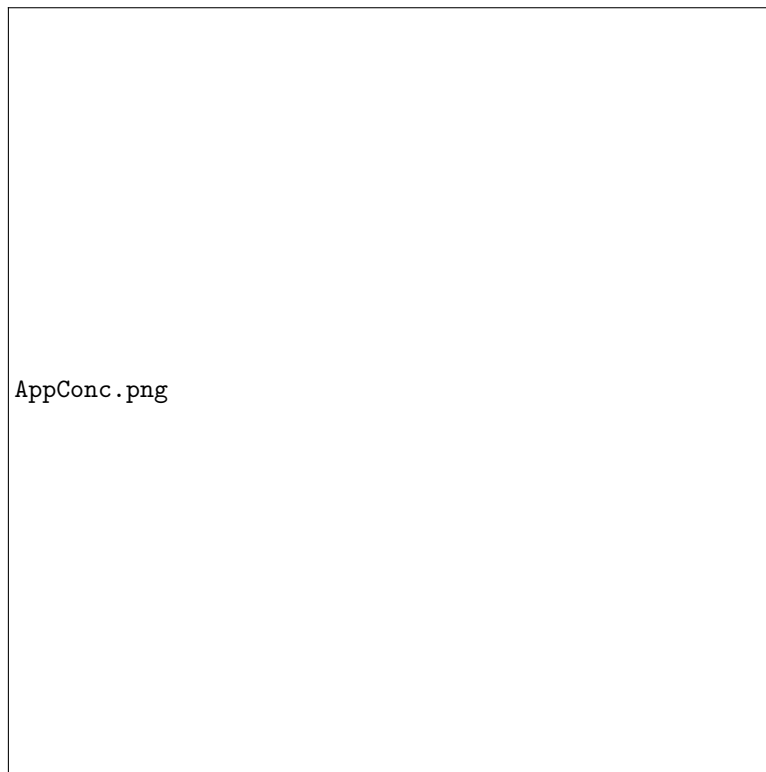
Conclusion

AppConc.png

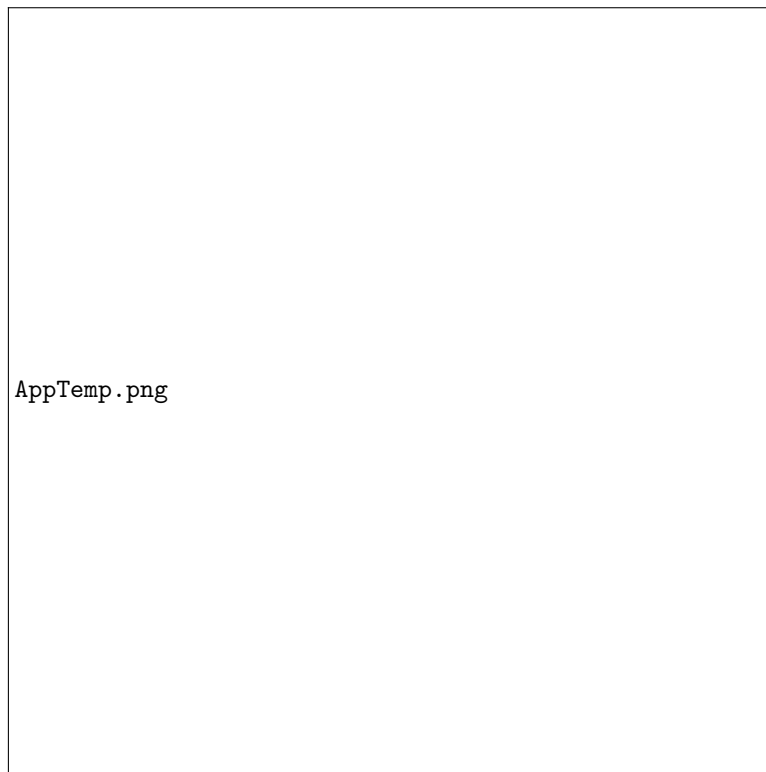Figure 8. Concentration Profile

AppTemp.png

Figure 9. Temperature Profile

# 6. References

Benavides, P. T. and Diwekar, U. (2012). Optimal control of biodiesel production in a batch reactor: Part ii: Stochastic control. *Fuel*, 94:218–226.

Bhoi, S., Lenka, M., and Sarkar, D. (2017). Particle engineering by optimization for the unseeded batch cooling crystallization of l-asparagine monohydrate. *CrystEngComm*, 19(42):6373–6382.

Corriou, J.-P. and Rohani, S. (2008). A new look at optimal control of a batch crystallizer. *AIChE journal*, 54(12):3188–3206.

Diwekar, U. (2008). *Introduction to applied optimization*, volume 22. Springer Science & Business Media.

Eugene, W. and Moshe, Z. (1965). On the relation between ordinary and stochastic differential equations. *International Journal of Engineering Science*, 3(2):213–229.

Feinberg, J. and Langtangen, H. P. (2015). Chaospy: An open source tool for designing methods of uncertainty quantification. *Journal of Computational Science*, 11:46–57.

Ghanem, R. and Spanos, P. D. (1990). Polynomial chaos in stochastic finite elements. *Journal of Applied Mechanics*, 57(1):197–202.

Ghanem, R. G. and Spanos, P. D. (1997). Spectral techniques for stochastic finite elements. *Archives of Computational Methods in Engineering*, 4(1):63–100.

Grosso, M., Cogoni, G., Baratti, R., and Romagnoli, J. A. (2011). Stochastic approach for the prediction of psd in crystallization processes: Formulation and comparative assessment of different stochastic models. *Industrial & Engineering Chemistry Research*, 50(4):2133–2143.

Hu, Q., Rohani, S., and Jutan, A. (2005). Modelling and optimization of seeded batch crystallizers. *Computers & chemical engineering*, 29(4):911–918.

Jones, A. (1974). Optimal operation of a batch cooling crystallizer. *Chemical Engineering Science*, 29(5):1075–1087.

Kim, K. K. K. and Braatz, R. D. (2012). Probabilistic analysis and control of uncertain dynamic systems: Generalized polynomial chaos expansion approaches. pages 44–49.

Kumar, D. and Budman, H. (2014). Robust nonlinear mpc based on volterra series and polynomial chaos expansions. *Journal of Process Control*, 24(1):304–317.

Lindenberg, C. and Mazzotti, M. (2011). Continuous precipitation of l-asparagine monohydrate in a micromixer: Estimation of nucleation and growth kinetics. *AIChE journal*, 57(4):942–950.

Ma, D. L., Chung, S. H., and Braatz, R. D. (1999). Worst-case performance analysis of optimal batch control trajectories. *AIChE journal*, 45(7):1469–1476.

Miller, S. M. and Rawlings, J. B. (1994). Model identification and control strategies for batch cooling crystallizers. *AIChE Journal*, 40(8):1312–1327.

Mullin, J. and Nỳvlt, J. (1971). Programmed cooling of batch crystallizers. *Chemical Engineering Science*, 26(3):369–377.

Nagy, Z. and Braatz, R. (2007). Distributional uncertainty analysis using power series and polynomial chaos expansions. *Journal of Process Control*, 17(3):229–240.

Paengjuntuek, W., Arpornwichanop, A., and Kittisupakorn, P. (2008). Product quality improvement of batch crystallizers by a batch-to-batch optimization and nonlinear control approach. *Chemical Engineering Journal*, 139(2):344–350.

Rawlings, J. B., Witkowski, W. R., and Eaton, J. W. (1992). Modelling and control of crystallizers. *Powder technology*, 69(1):3–9.

Rico-Ramirez, V. and Diwekar, U. M. (2004). Stochastic maximum principle for optimal control under uncertainty. *Computers & Chemical Engineering*, 28(12):2845–2849.

Shi, D., El-Farra, N. H., Li, M., Mhaskar, P., and Christofides, P. D. (2006). Predictive control of particle size distribution in particulate processes. *Chemical Engineering Science*, 61(1):268–281.

Yenkie, K. M. and Diwekar, U. (2012). Stochastic optimal control of seeded batch crystallizer applying the ito process. *Industrial & Engineering Chemistry Research*, 52(1):108–122.