Optimal designs for the methane flux in troposphere

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Abstract

The understanding of methane emission and methane absorption plays a central role both in the atmosphere and on the surface of the Earth. Several important ecological processes, e.g., ebullition of methane and its natural microergodicity request better designs for observations in order to decrease variability in parameter estimation. Thus, a crucial fact, before the measurements are taken, is to give an optimal design of the sites where observations should be collected in order to stabilize the variability of estimators. In this paper we introduce a realistic parametric model of covariance and provide theoretical and numerical results on optimal designs. For parameter estimation D-optimality, while for prediction integrated mean square error and entropy criteria are used. We illustrate applicability of obtained benchmark designs for increasing/measuring the efficiency of the engineering designs for estimation of methane rate in various temperature ranges and under different correlation parameters. We show that in most situations these benchmark designs have higher efficiency.

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1. Introduction

The understanding of methane emission and methane absorption plays a central role both in the atmosphere (for troposphere see, e.g., [32]) and on the surface of the Earth (see, e.g., [20] regarding the methane emissions from natural wetlands and references therein or [14] for efficient and robust model of the methane emission from sedge-grass marsh in South Bohemia). Several important ecological processes, e.g., ebullition of methane and its natural microergodicity request better designs for observations in order to decrease variability in parameter estimation [15]. In this context by a design we mean a set of locations where the investigated process is observed. Thus, a crucial fact, before the measurements are taken, is to give an optimal design of the sites where observations should be collected. Rodríguez-Díaz et al. [27] provided a comparison of filling and D-optimal designs for a one-dimensional design variable, e.g., temperature. However, such a model oversimplifies the important fact that variation of other variables, e.g., rates k_1 of the considered modified Arrhenius model, could disturb the efficiency of the learning process. The latter statement is also in agreement with common sense in physical chemistry. In this paper the difficulties of modelling and design are treated, mainly by allowing an Ornstein-Uhlenbeck (OU) sheet error model.

We concentrate on efficient estimation of the parameters of the modified Arrhenius model (model popular in chemical kinetics), which is used by Vaghjiani and Ravishankara [32] as a flux model of methane in troposphere. This generalized exponential (GE) model can be expressed as

$$Y = Ax^{\mu}\mathrm{e}^{-Bx} + \epsilon = \eta(x, \mu, B) + \epsilon, \tag{1.1}$$

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where $A, B, \mu \in \mathbb{R},\ A,\ B \geq 0$, are constants and ε is a random error term. In the case of correlated errors such a model was studied by Rodríguez-Díaz et al. [27], however, in that work error structures were univariate stochastic processes. In [26] and [27] the authors concentrated on the Modified-Arrhenius (MA) model, which is equivalent to the GE model through the change of variable $x = 1/t$. This model is useful for chemical kinetic mainly because it is a generalization of Arrhenius model describing the influence of temperature t on the rates of chemical processes, see, e.g., [18] for general discussion and [25] for optimal designs. However, for specific setups, for instance, long temperature ranges, Arrhenius model is insufficient and the Modified Arrhenius (or GE model) appears to be the good alternative [see for instance 11]. Other applications of model (1.1) in chemistry are related to the transition state theory (TST) of chemical reactions [13].

In practical chemical kinetics two steps are taken: first the rates k_1 are estimated (typically with symmetric estimated error) and then modified Arrhenius model is fitted to the rates, i.e.,

$$k_1 = A(1/t)^{\mu} \mathrm{e}^{-B/t} + \widetilde{\varepsilon}(t). \tag{1.2}$$

Statistically correct would be to assess both steps by one optimal experimental planning. Rodríguez-Díaz et al. [27] concentrated on the second phase, i.e., what is the optimal distribution of temperature for obtaining statistically efficient estimators of trend parameters $A, B,\ \mu$ and correlation parameters of the error term $\widetilde{\varepsilon}$. In this paper we provide designs both for rates and temperatures, and in this way substantially generalize the previously studied model.

Correlation is the natural dependence measure fitting for elliptically symmetric distributions (e.g., Gaussian). By taking s (this variable can play, for example, the role of atmospheric pressure, latitude or location of the measuring balloon in troposphere, either vertically or horizontally) and temperature t to be variables of covariance, our model (1.1) takes a form of a stationary process

$$Y(s,t) = k_1 + \varepsilon(s,t), \tag{1.3}$$

where the design points are taken from a compact design space $\mathcal{X} = [a_1, b_1] \times [a_2, b_2]$, with $b_1 > a_1$ and $b_2 > a_2$, and $\varepsilon(s,t),\ s,t \in \mathbb{R}$, is a stationary OU sheet, that is a zero mean Gaussian process with covariance structure

$$\mathsf{E}\,\varepsilon(s_1,t_1)\varepsilon(s_2,t_2) = \frac{\widetilde{\sigma}^2}{4\alpha\beta} \exp\big(-\alpha|s_1 - s_2| - \beta|t_1 - t_2|\big), \tag{1.4}$$

where $\alpha > 0,\ \beta > 0,\ \widetilde{\sigma} > 0$. We remark that $\varepsilon(s,t)$ can also be represented as

$$\varepsilon(s,t) = \frac{\widetilde{\sigma}}{2\sqrt{\alpha\beta}} \mathrm{e}^{-\alpha s - \beta t} \mathcal{W}\big(\mathrm{e}^{2\alpha s}, \mathrm{e}^{2\beta t}\big),$$

where $\mathcal{W}(s,t),\ s,t \in \mathbb{R}$, is a standard one-dimensional Brownian sheet [4, 5]. Covariance structure (1.4) implies that for $\mathbf{d} = (d,\delta),\ d \geq 0,\ \delta \geq 0$, the variogram $2\gamma(\mathbf{d}) := \mathrm{Var}\big(\varepsilon(s+d, t+\delta) - \varepsilon(s,t)\big)$ equals

$$2\gamma(\mathbf{d}) = \frac{\widetilde{\sigma}^2}{2\alpha\beta}\Big(1 - \mathrm{e}^{-\alpha d - \beta\delta}\Big)$$

and the correlation between two measurements depends on the distance through the semivariogram $\gamma(\mathbf{d})$.

As can be visible from relation (1.2) between rates and parameters A, μ and B of the modified Arrhenius model, the second variable s is missing from trend since it is not chemically understood as driving mechanism of chemical kinetics, however, in this context it is an environment variable.

In order to apply the usual notations of spatial modeling [17] we introduce $\sigma := \widetilde{\sigma}/(2\sqrt{\alpha\beta})$ and instead of (1.4) we investigate

$$\mathsf{E}\,\varepsilon(s_1,t_1)\varepsilon(s_2,t_2) = \sigma^2 \exp\big(-\alpha|s_1 - s_2| - \beta|t_1 - t_2|\big), \tag{1.5}$$

where σ is considered as a nuisance parameter.

We remark that in order to reduce the length of the paper proofs of all theorems presented here together with calculations corresponding to Examples 2.8 and 3.5 are given in a separate Supplementary section which is available on the website of the publisher. These details can also be found in [7].

2. Benchmarking grid designs for the OU sheet with constant trend

In this section we derive several optimal design results for the case of constant trend and regular grids resulting in a Kronecker product covariance structure. These theoretical contributions will serve as benchmarks for optimal designs in a methane flux model. Thus we consider the stationary process

$$Y(s,t) = \theta + \varepsilon(s,t) \tag{2.1}$$

with the design points taken from a compact design space $\mathcal{X} = [a_1, b_1] \times [a_2, b_2]$, where $b_1 > a_1$ and $b_2 > a_2$ and $\varepsilon(s,t),\ s,t \in \mathbb{R}$, is a stationary Ornstein-Uhlenbeck sheet, i.e., a zero mean Gaussian process with covariance structure (1.5).

2.1. D-optimality

As a first step we derive D-optimal designs, that is arrangements of design points that maximize the objective function $\Phi(M) := \det(M)$, where M is the Fisher information matrix of observations of the random field Y. This method, "plugged" from the widely developed uncorrelated setup, is offering considerable potential for automatic implementation, although further development is needed before it can be applied routinely in practice. Theoretical justifications of using the Fisher information for D-optimal designing under correlation can be found in [1, 24] and [31].

We investigate grid designs of the form $\big\{(s_i, t_j) :\ i = 1, 2, \ldots, n,\ j = 1, 2, \ldots, m\big\} \subset \mathcal{X} = [a_1, b_1] \times [a_2, b_2]$, $n, m \geq 2$, and without loss of generality we may assume $a_1 \leq s_1 < s_2 < \ldots < s_n \leq b_1$ and $a_2 \leq t_1 < t_2 < \ldots < t_m \leq b_2$. Usually, the grid containing the design points can be arranged arbitrary in the design space $\mathcal{X}$, but we also consider restricted D-optimality, when $s_1 = a_1,\ s_n = b_1$ and $t_1 = a_2,\ t_m = b_2$, i.e., the vertices of $\mathcal{X}$ are included in all designs.

2.1.1. Estimation of trend parameter only

Let us assume first that parameters α, β and σ of the covariance structure (1.5) of the OU sheet ε are given and we are interested in estimation of the trend parameter θ. In this case the Fisher information on θ based on observations $\big\{Y(s_i, t_j),\ i = 1, 2, \ldots, n,\ j = 1, 2, \ldots, m\big\}$ equals $M_\theta(n, m) = \mathbf{1}_{nm}^\top C^{-1}(n, m, r)\mathbf{1}_{nm}$, where $\mathbf{1}_k,\ k \in \mathbb{N}$, denotes the column vector of ones of length k, $r = (\alpha, \beta)^\top$, and $C(n, m, r)$ is the covariance matrix of the observations [24, 33]. Further, let $d_i := s_{i+1} - s_i,\ \ i = 1, 2, \ldots, n-1$, and $\delta_j := t_{j+1} - t_j,\ j = 1, 2, \ldots, m-1$, be the directional distances between two adjacent design points. With the help of this representation one can prove the following theorem.

Theorem 2.1 *Consider the OU model* (2.1) *with covariance structure* (1.5) *observed in points* $\big\{(s_i, t_j),\ i = 1, 2, \ldots, n,\ j = 1, 2, \ldots, m\big\}$ *and assume that the only parameter of interest is the trend parameter* θ*. In this case*

$$M_\theta(n, m) = \left(1 + \sum_{i=1}^{n-1} \frac{1 - p_i}{1 + p_i}\right)\left(1 + \sum_{j=1}^{m-1} \frac{1 - q_j}{1 + q_j}\right), \tag{2.2}$$

where $p_i := \exp(-\alpha d_i),\ q_j := \exp(-\beta\delta_j),\ i = 1, 2, \ldots, n-1,\ j = 1, 2, \ldots, m-1$*, and the directionally equidistant design* $d_1 = d_2 = \ldots = d_{n-1}$ *and* $\delta_1 = \delta_2 = \ldots = \delta_{m-1}$ *is optimal for estimation of* θ*.*

2.1.2. Estimation of covariance parameters only

Assume now that we are interested only in the estimation of the parameters α and β of the Ornstein-Uhlenbeck sheet. According to the results of Pázman [24] and Xia et al. [33] the Fisher information matrix on $r = (\alpha, \beta)^\top$ has the form

$$M_r(n, m) = \begin{bmatrix} M_\alpha(n, m) & M_{\alpha,\beta}(n, m) \\ M_{\alpha,\beta}(n, m) & M_\beta(n, m) \end{bmatrix}, \tag{2.3}$$

where

$$M_\alpha(n,m) := \frac{1}{2}\mathrm{tr}\left\{C^{-1}(n,m,r)\frac{\partial C(n,m,r)}{\partial \alpha}C^{-1}(n,m,r)\frac{\partial C(n,m,r)}{\partial \alpha}\right\},$$
$$M_\beta(n,m) := \frac{1}{2}\mathrm{tr}\left\{C^{-1}(n,m,r)\frac{\partial C(n,m,r)}{\partial \beta}C^{-1}(n,m,r)\frac{\partial C(n,m,r)}{\partial \beta}\right\},$$
$$M_{\alpha,\beta}(n,m) := \frac{1}{2}\mathrm{tr}\left\{C^{-1}(n,m,r)\frac{\partial C(n,m,r)}{\partial \alpha}C^{-1}(n,m,r)\frac{\partial C(n,m,r)}{\partial \beta}\right\},$$

and $C(n,m,r)$ is the covariance matrix of the observations $\big\{Y(s_i,t_j),\ i{=}1,2,\ldots,n,\ j{=}1,2,\ldots,m\big\}$. Note that here $M_\alpha(n,m)$ and $M_\beta(n,m)$ are Fisher information on parameters α and β, respectively, taking the other parameter as a nuisance.

The following theorem gives the exact form of $M_r(n,m)$ for the model (2.1).

Theorem 2.2 *Consider the OU model* (2.1) *with covariance structure* (1.5) *observed in points* $\big\{(s_i,t_j),\ i=1,2,\ldots,n,\ j=1,2,\ldots,m\big\}$. *Then*

$$M_\alpha(n,m) = m\sum_{i=1}^{n-1}\frac{d_i^2p_i^2(1+p_i^2)}{(1-p_i^2)^2}, \qquad M_\beta(n,m) = n\sum_{j=1}^{m-1}\frac{\delta_j^2q_j^2(1+q_j^2)}{(1-q_j^2)^2}, \tag{2.4}$$
$$M_{\alpha,\beta}(n,m) = 2\Big(\sum_{i=1}^{n-1}\frac{d_ip_i^2}{1-p_i^2}\Big)\Big(\sum_{j=1}^{m-1}\frac{\delta_jq_j^2}{1-q_j^2}\Big),$$

where d_i,δ_j *and* p_i,q_j *denote the same quantities as before, that is,* $d_i := s_{i+1}-s_i,\ \delta_j := t_{j+1}-t_j$ *and* $p_i := \exp(-\alpha d_i),\ q_j := \exp(-\beta\delta_j),\ i=1,2,\ldots,n-1,\ j=1,2,\ldots,m-1$.

Remark 2.3 Observe that Fisher information on a single parameter (α or β) depends only on the design points corresponding to that particular parameter, e.g., $M_\alpha(n,m) = mM_\alpha(n)$, where $M_\alpha(n)$ is the Fisher information corresponding to the covariance parameter α of a stationary OU process observed in design points $\{s_i,\ i=1,2,\ldots,n\}$ of the interval $[a_1,b_1]$.

Now, with the help of Theorem 2.2 one can formulate a result on the restricted D-optimal design for the parameters of the covariance structure of the OU sheet.

Theorem 2.4 *The restricted design which is D-optimal for estimation of the covariance parameters* $\alpha,\ \beta$ *does not exist within the class of admissible designs.*

From the point of view of a chemometrician, Theorem 2.4 points out that microergodicity should be added to the model in order to obtain regular designs. Several ways are possible, for instance, nugget effect or compounding [see, e.g., 23].

Example 2.5 Without loss of generality one may assume that the design space is $\mathcal{X} = [0,1]^2$. Let $\alpha = 0.6,\ \beta = 1$, and consider the case $n = m = 3$ where $s_1 = t_1 = 0,\ s_2 := d,\ t_2 := \delta,\ s_3 = t_3 = 1$. For this particular restricted design we obviously have $d_1 = d,\ d_2 = 1-d,\ \delta_1 = \delta,\ \delta_2 = 1-\delta$. In Figure 1, where $\det\big(M_r(3,3)\big)$ is plotted as function of d and δ, one can clearly see that the maximal information is gained at the frontier points, when either $d\in\{0,1\}$ or $\delta\in\{0,1\}$.

Now, let us have a look at the free boundary directionally equidistant designs, that is at designs where $d_1 = d_2 = \ldots = d_{n-1} =: d$ and $\delta_1 = \delta_2 = \ldots = \delta_{m-1} =: \delta$. In this case a D-optimal design is specified by directional distances d and δ which maximize

$$\det\big(M_r(n,m)\big) = \frac{(n-1)(m-1)d^2\delta^2}{\big(\mathrm{e}^{2\alpha d}-1\big)^2\big(\mathrm{e}^{2\beta\delta}-1\big)^2}\Big(nm\big(\mathrm{e}^{2\alpha d}+1\big)\big(\mathrm{e}^{2\beta\delta}+1\big) - 4(n-1)(m-1)\Big). \tag{2.5}$$

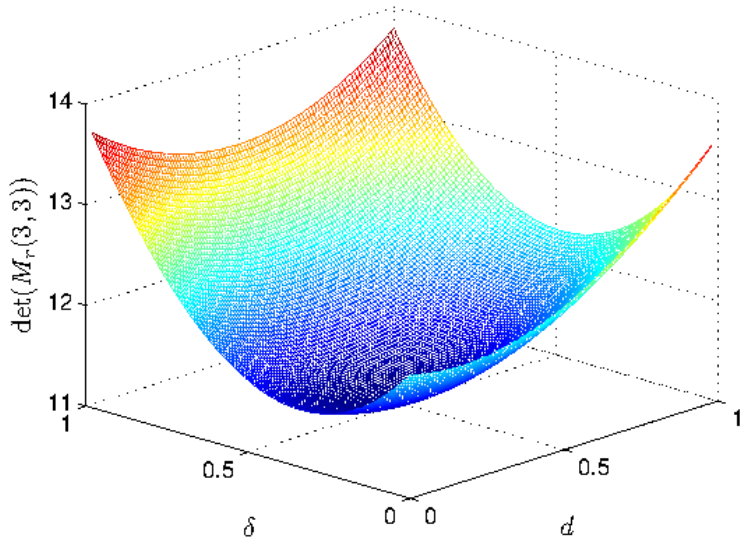

Figure 1: Fisher information on correlation parameters (α, β) for $n = m = 3$ as function of $d = d_1$ and $\delta = \delta_1$ for $\alpha = 0.6,\ \beta = 1$.

In case of OU processes this question does not appear, since for processes Fisher information on covariance parameter based on n equidistant design points depends linearly on the two-point design Fisher information [17].

Theorem 2.6 *If* $nm \geq 2(n-1)(m-1)$ *then* $\det\big(M_r(n,m)\big)$ *is strictly monotone decreasing both in* d *and* δ*, so its maximum is reached at* $d = \delta = 0$*. If* $nm < 2(n-1)(m-1)$ *then for fixed and small enough* d *(*δ*), function* $\det\big(M_r(n,m)\big)$ *has a single maximum in* δ *(*d*).*

Remark 2.7 Observe that for $1 < n = m \in \mathbb{N}$, condition $nm \geq 2(n-1)(m-1)$ is equivalent to $n \leq 3$. Further, if $nm \leq 2(n-1)(m-1)$ then the statement of Theorem 2.6 does not imply the existence of a D-optimal design. Figure 2 shows that the extremal point of $\det\big(M_r(n,m)\big)$ can be a saddle point and the maximum is reached when either $d = 0$ or $\delta = 0$.

2.1.3. Estimation of all parameters

Consider now the most general case, when both $\alpha,\ \beta$ and θ are unknown and the Fisher information matrix on these parameters equals

$$M(n,m) = \begin{bmatrix} M_\theta(n,m) & 0 \\ 0 & M_r(n,m) \end{bmatrix},$$

where $M_\theta(n,m)$ and $M_r(n,m)$ are Fisher information matrices on θ and $r = (\alpha,\beta)^\top$, respectively, see (2.2) and (2.3). Thus, the objective function to be maximized is $\det\big(M(n,m)\big) = M_\theta(n,m)\det\big(M_r(n,m)\big)$.

Example 2.8 Consider the nine-point restricted design of Example 2.5, that is $\mathcal{X} = [0,1]^2,\ n = m = 3$ and $s_1 = t_1 = 0,\ s_2 := d,\ t_2 := \delta,\ s_3 = t_3 = 1$, implying $d_1 = d,\ d_2 = 1-d,\ \delta_1 = \delta,\ \delta_2 = 1-\delta$. In this case

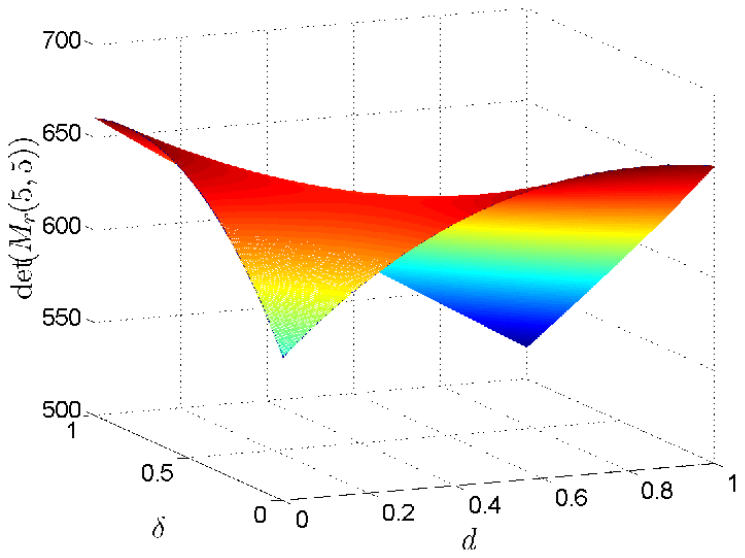

Figure 2: Fisher information of boundary free design on correlation parameters (α, β) for $n = m = 5$ and $\alpha = 1,\ \beta = 1$.

from (2.2) and (2.4) we have

$$\begin{aligned}\det\big(M(3,3)\big) = &\left(1+\frac{\mathrm{e}^{\alpha d}-1}{\mathrm{e}^{\alpha d}+1}+\frac{\mathrm{e}^{\alpha(1-d)}-1}{\mathrm{e}^{\alpha(1-d)}+1}\right)\left(1+\frac{\mathrm{e}^{\beta\delta}-1}{\mathrm{e}^{\beta\delta}+1}+\frac{\mathrm{e}^{\beta(1-\delta)}-1}{\mathrm{e}^{\beta(1-\delta)}+1}\right)\\ &\times\left(9\left(\frac{d^2\big(\mathrm{e}^{2\alpha d}+1\big)}{\big(\mathrm{e}^{2\alpha d}-1\big)^2}+\frac{(1-d)^2\big(\mathrm{e}^{2\alpha(1-d)}+1\big)}{\big(\mathrm{e}^{2\alpha(1-d)}-1\big)^2}\right)\left(\frac{\delta^2\big(\mathrm{e}^{2\beta\delta}+1\big)}{\big(\mathrm{e}^{2\beta\delta}-1\big)^2}+\frac{(1-\delta)^2\big(\mathrm{e}^{2\beta(1-\delta)}+1\big)}{\big(\mathrm{e}^{2\beta(1-\delta)}-1\big)^2}\right)\right.\\ &\left.-4\left(\frac{d}{\mathrm{e}^{2\alpha d}-1}+\frac{1-d}{\mathrm{e}^{2\alpha(1-d)}-1}\right)^2\left(\frac{\delta}{\mathrm{e}^{2\beta\delta}-1}+\frac{1-\delta}{\mathrm{e}^{2\beta(1-\delta)}-1}\right)^2\right).\end{aligned}\tag{2.6}$$

Tedious calculations show that $\det\big(M(3,3)\big)$ has a single global minimum at $d = \delta = 1/2$, while the maximum is reached at the four vertices of $\mathcal{X}$, namely at $(0,0)$, $(0,1)$, $(1,0)$ and $(1,1)$. In this way a restricted D-optimal design does not exist.

Again, let us also have a look at the free boundary directionally equidistant designs with directional distances d and δ. The objective function to be maximized in order to get the D-optimal design is

$$\begin{aligned}\det\big(M(n,m)\big) = &\frac{(n-1)(m-1)d^2\delta^2}{\big(\mathrm{e}^{2\alpha d}-1\big)^2\big(\mathrm{e}^{2\beta\delta}-1\big)^2\big(\mathrm{e}^{\alpha d}+1\big)\big(\mathrm{e}^{\beta\delta}+1\big)}\big(n(\mathrm{e}^{\alpha d}-1)+2\big)\big(m(\mathrm{e}^{\beta\delta}-1)+2\big)\\ &\times\Big(nm\big(\mathrm{e}^{2\alpha d}+1\big)\big(\mathrm{e}^{2\beta\delta}+1\big)-4(n-1)(m-1)\Big).\end{aligned}\tag{2.7}$$

For simplicity assume $n = m$.

Theorem 2.9 *If $n = 2$ then $\det\big(M(n,n)\big)$ is strictly monotone decreasing both in d and δ, so its maximum is reached at $d = \delta = 0$. If $n \geq 3$ then $\det\big(M(n,n)\big)$ has a global maximum at (d^*, δ^*) which solves*

$$n^2\big(\mathrm{e}^{2\beta\delta}+1\big)g_1(\alpha d, n) = 4(n-1)^2 g_2(2\alpha d, n), \qquad n^2\big(\mathrm{e}^{2\alpha d}+1\big)g_1(\beta\delta, n) = 4(n-1)^2 g_2(\beta\delta, n),\tag{2.8}$$

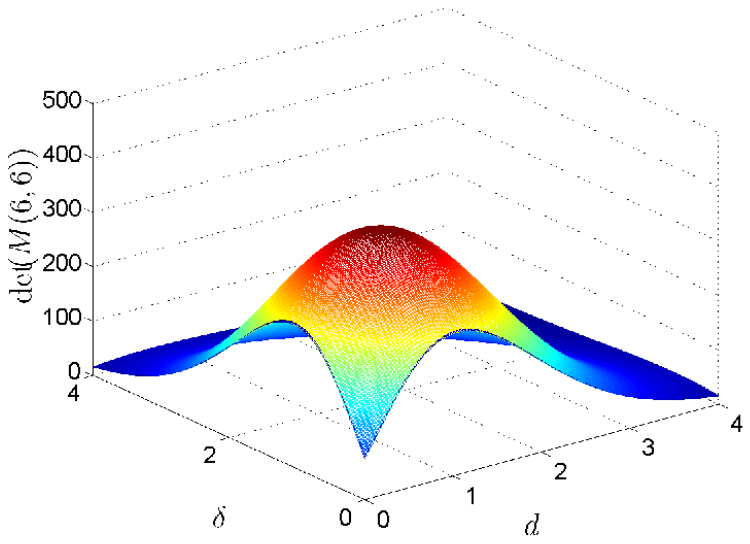

Figure 3: Fisher information of boundary free design on all parameters for $n = m = 6$ and $\alpha = 1,\ \beta = 1$.

where

$$g_1(x,n) := \mathrm{e}^{5x}n(1-x) + \mathrm{e}^{4x}(2nx - 3x - n + 2) + \mathrm{e}^{3x}x(1-4n) + \mathrm{e}^{2x}x(4n-7) + \mathrm{e}^{x}(x - n - nx) + n - 2,$$
$$g_2(x,n) := \mathrm{e}^{3x}n(1-2x) + \mathrm{e}^{2x}(3nx - 5x + 2 - n) + \mathrm{e}^{x}(x - n - nx) + n - 2. \tag{2.9}$$

Theorem 2.9 shows that the situation here completely differs from the case when only covariance parameters are estimated and an optimal free boundary directionally equidistant design does exist. This can clearly be observed on Figure 3 showing $\det\big(M(6,6)\big)$ for $\alpha = 1,\ \beta = 1$. Further, simulation results show that for all $n \geq 3$ objective function $\det\big(M(n,n)\big)$ has a unique maximal point (system (2.8) has a unique solution), however, a rigorous proof of this fact have not been found yet.

2.2. Optimal design with respect to IMSPE criterion

As before, suppose we have observations $\big\{Y(s_i,t_j),\ i = 1,2,\ldots,n,\ j = 1,2,\ldots,m\big\}$. The main aim of the kriging technique consists of the prediction of the output of the simulator on the experimental region. For any untried location $(x_1,x_2) \in \mathcal{X}$ the estimation procedure is focused on the best linear unbiased estimator of $Y(x_1,x_2)$ given by $\widehat{Y}(x_1,x_2) = \widehat{\theta} + R^{\top}(x_1,x_2)C^{-1}(n,m,r)(\mathbf{Y} - \mathbf{1}_{nm}\widehat{\theta})$, where $\mathbf{Y} = \big(Y(s_1,t_1), Y(s_1,t_2), \ldots, Y(s_n,t_m)\big)^{\top}$ is the vector of observations, $\widehat{\theta}$ is the generalized least squares estimator of θ, that is $\widehat{\theta} = \big(\mathbf{1}_{nm}^{\top}C^{-1}(n,m,r)\mathbf{1}_{nm}\big)^{-1}\mathbf{1}_{nm}^{\top}C^{-1}(n,m,r)\mathbf{Y}$, and $R(x_1,x_2)$ is the vector of correlations between $Y(x_1,x_2)$ and vector $\mathbf{Y}$, which has the form $R(x_1,x_2) = \big(\varrho(x_1,x_2,s_1,t_1),\ldots,\varrho(x_1,x_2,s_i,t_j),\ldots,\varrho(x_1,x_2,s_n,t_m)\big)^{\top}$, where $\varrho(x_1,x_2,s_i,t_j) := \varrho_1(x_1,s_i)\varrho_2(x_2,t_j)$ with components $\varrho_1(x_1,s_i) := \exp\big(-\alpha|x_1 - s_i|\big)$ and $\varrho_2(x_2,t_j) := \exp\big(-\beta|x_2 - t_j|\big)$. Usually, correlation parameters α,β are unknown and will be estimated by maximum likelihood method. Thus, the kriging predictor is obtained by substituting the maximum likelihood estimators (MLE) $(\widehat{\alpha},\widehat{\beta})$ for (α,β) and in such a case $\widehat{Y}(x_1,x_2)$ is called the MLE-empirical best linear unbiased predictor [29].

In this way a natural criterion of optimality will minimize suitable functionals of the Mean Squared

Prediction Error (MSPE) given by

$$\mathrm{MSPE}\big(\widehat{Y}(x_1,x_2)\big) := \sigma^2\left[1-\big(1,\,R^\top(x_1,x_2)\big)\left[\begin{array}{c:c}0 & \mathbf{1}_{nm}^\top \\ \hdashline \mathbf{1}_{nm} & C(n,m,r)\end{array}\right]^{-1}\big(1,\,R^\top(x_1,x_2)\big)^\top\right]. \tag{2.10}$$

Since the prediction accuracy is often related to the entire prediction region $\mathcal{X}$, the design criterion IMSPE is given by

$$\mathrm{IMSPE}\big(\widehat{Y}\big) := \sigma^{-2}\iint\limits_{\mathcal{X}} \mathrm{MSPE}\big(\widehat{Y}(x_1,x_2)\big)\,\mathrm{d}x_1\,\mathrm{d}x_2.$$

Theorem 2.10 *Let us assume that the design space $\mathcal{X}=[0,1]^2$ and since extrapolative prediction is not advisable in kriging, we can set $s_1=t_1=0$ and $s_n=t_m=1$.*

$$\begin{aligned}\mathrm{MSPE}\big(\widehat{Y}(x_1,x_2)\big) = \sigma^2\Bigg[1-&\left(\varrho_1^2(x_1,s_n)+\sum_{i=1}^{n-1}\frac{\big(\varrho_1(x_1,s_i)-\varrho_1(x_1,s_{i+1})p_i\big)^2}{1-p_i^2}\right)\\ &\times\left(\varrho_2^2(x_2,t_m)+\sum_{j=1}^{m-1}\frac{\big(\varrho_2(x_2,t_j)-\varrho_2(x_2,t_{j+1})q_j\big)^2}{1-q_j^2}\right)\\ +\left(1+\sum_{i=1}^{n-1}\frac{1-p_i}{1+p_i}\right)^{-1}&\left(1+\sum_{j=1}^{m-1}\frac{1-q_j}{1+q_j}\right)^{-1}\left(1-\left(\varrho_1(x_1,s_n)+\sum_{i=1}^{n-1}\frac{\varrho_1(x_1,s_i)-\varrho_1(x_1,s_{i+1})p_i}{1+p_i}\right)\right.\\ &\left.\times\left(\varrho_2(x_2,t_m)+\sum_{j=1}^{m-1}\frac{\varrho_2(x_2,t_j)-\varrho_2(x_2,t_{j+1})q_j}{1+q_j}\right)\right)^2\Bigg],\end{aligned} \tag{2.11}$$

where again $p_i := \exp(-\alpha d_i)$, $q_j := \exp(-\beta\delta_j)$ with $d_i := s_{i+1}-s_i$ and $\delta_j := t_{j+1}-t_j$, $i=1,2,\ldots,n-1$, $j=1,2,\ldots,m-1$. Further,

$$\begin{aligned}\mathrm{IMSPE}\big(\widehat{Y}\big) = 1-&\left(\frac{n-1}{\alpha}-2\sum_{i=1}^{n-1}\frac{d_i p_i^2}{1-p_i^2}\right)\left(\frac{m-1}{\beta}-2\sum_{j=1}^{m-1}\frac{\delta_j q_j^2}{1-q_j^2}\right)\\ &+\left(1+\sum_{i=1}^{n-1}\frac{1-p_i}{1+p_i}\right)^{-1}\left(1+\sum_{j=1}^{m-1}\frac{1-q_j}{1+q_j}\right)^{-1}\left[1-\frac{8}{\alpha\beta}\left(\sum_{i=1}^{n-1}\frac{1-p_i}{1+p_i}\right)\left(\sum_{j=1}^{m-1}\frac{1-q_j}{1+q_j}\right)\right.\\ &\left.+\left(\sum_{i=1}^{n-1}\frac{1-p_i^2+2\alpha d_i p_i}{\alpha(1+p_i)^2}\right)\left(\sum_{j=1}^{m-1}\frac{1-q_j^2+2\beta\delta_j q_j}{\beta(1+q_j)^2}\right)\right].\end{aligned} \tag{2.12}$$

For any sample size the directionally equidistant design $d_1=d_2=\ldots=d_{n-1}$ and $\delta_1=\delta_2=\ldots=\delta_{m-1}$ is optimal with respect to the IMSPE criterion.

Remark 2.11 We remark that (2.12) is an extension of the IMSPE criterion for the classical OU process given by Baldi Antognini and Zagoraiou [3, Proposition 4.1], while the optimality result generalizes Proposition 4.2 of [3].

2.3. Optimal design with respect to entropy criterion

Another possible approach to optimal design is to find locations which maximize the amount of obtained information. Following the ideas of Shewry and Wynn [30] one has to maximize the entropy $\mathrm{Ent}(\mathbf{Y})$ of the observations corresponding to the chosen design, which in the Gaussian case form an nm-dimensional normal vector with covariance matrix $\sigma^2\,C(n,m,r)$, that is

$$\mathrm{Ent}(\mathbf{Y}) = \frac{nm}{2}\big(1+\ln(2\pi\sigma^2)\big)+\frac{1}{2}\ln\det C(n,m,r).$$

Theorem 2.12 *In our setup entropy* $\mathrm{Ent}(\mathbf{Y})$ *has the form*

$$\mathrm{Ent}(\mathbf{Y}) = \frac{nm}{2}\big(1+\ln(2\pi\sigma^2)\big) + \frac{m}{2}\sum_{i=1}^{n-1}\ln\big(1-p_i^2\big) + \frac{n}{2}\sum_{j=1}^{m-1}\ln\big(1-q_j^2\big). \tag{2.13}$$

For any sample size the directionally equidistant design $d_1 = d_2 = \ldots = d_{n-1}$ *and* $\delta_1 = \delta_2 = \ldots = \delta_{m-1}$ *is optimal with respect to the entropy criterion.*

3. D-optimal designs for the Arrhenius model with OU error

In the present section we derive objective functions for D-optimal designs for estimating parameters of the Arrhenius model (1.1). We consider the stationary process

$$Y(s,t) = \big(A/t^{\mu}\big)\mathrm{e}^{-B/t} + \varepsilon(s,t), \tag{3.1}$$

observed on a compact design space $\mathcal{X} = [a_1,b_1]\times[a_2,b_2]$, where $b_1 > a_1$ and $b_2 > a_2$ and $\varepsilon(s,t),\ s,t\in\mathbb{R}$, is again a stationary Ornstein-Uhlenbeck sheet, that is a zero mean Gaussian process with covariance structure (1.5). Since parameter A is usually known, without loss of generality we may assume $A = 1$ and consider model (3.1) with trend function $\eta(s,t;\mu,B) := \big(1/t^{\mu}\big)\mathrm{e}^{-B/t}$.

From the point of view of applications we distinguish two important cases.

- Rate μ is known, which is an assumption made by several authors, see, e.g., [12]. The uncorrelated case has already been studied by Rodríguez-Díaz and Santos-Martín [26], where the authors proved that for approximated designs a two-point design is optimal.

- Rate μ is unknown and one has to estimate it together with B. For this model the uncorrelated case has also been studied, Rodríguez-Díaz et al. [27] considered both equidistant and general designs.

3.1. Estimation of trend

Assume that covariance parameters α,β and σ of the OU sheet and rate μ of the Arrhenius model are given and we are interested in estimation of the trend parameter B. The Fisher information on B based on observations $\big\{Y(s_i,t_j),\ i=1,2,\ldots,n,\ j=1,2,\ldots,m\big\}$ of the process (3.1) equals $M_B(n,m) = F^{\top}(n,m,B)C^{-1}(n,m,r)F^{\top}(n,m,B)$, where

$$F(n,m,B) := \left(\frac{\eta(s_1,t_1;\mu,B)}{\partial B}, \frac{\eta(s_1,t_2;\mu,B)}{\partial B}, \ldots, \frac{\eta(s_n,t_m;\mu,B)}{\partial B}\right)^{\top}.$$

Theorem 3.1 *In our setup*

$$M_B(n,m) = \left(1+\sum_{i=1}^{n-1}\frac{1-p_i}{1+p_i}\right)\left(\kappa_m^2 + \sum_{j=1}^{m-1}\frac{(\kappa_j-\kappa_{j+1}q_j)^2}{1-q_j^2}\right), \tag{3.2}$$

where $\kappa_j := -\exp\big(-B/t_j\big)/t_j^{\mu+1}$ *if* $t_j\neq 0$, *and* $\kappa_j := 0$, *otherwise.*

In case one has to estimate both μ and B, the objective function to be maximized in order to get the D-optimal design is $\det\big(M_{\mu,B}(n,m)\big)$, where again $M_{\mu,B}(n,m) = G^{\top}(n,m,\mu,B)C^{-1}(n,m,r)G^{\top}(n,m,\mu,B)$ with

$$G(n,m,\mu,B) := \begin{bmatrix} \frac{\eta(s_1,t_1;\mu,B)}{\partial\mu} & \frac{\eta(s_1,t_2;\mu,B)}{\partial\mu} & \cdots & \frac{\eta(s_n,t_m;\mu,B)}{\partial\mu} \\ \frac{\eta(s_1,t_1;\mu,B)}{\partial B} & \frac{\eta(s_1,t_2;\mu,B)}{\partial B} & \cdots & \frac{\eta(s_n,t_m;\mu,B)}{\partial B} \end{bmatrix}^{\top}.$$

Theorem 3.2 *In our setup*

$$M_{\mu,B}(n,m) = \left(1 + \sum_{i=1}^{n-1} \frac{1-p_i}{1+p_i}\right) \times \begin{bmatrix} \lambda_m^2 + \sum_{j=1}^{m-1} \frac{(\lambda_j - \lambda_{j+1}q_j)^2}{1-q_j^2} & \lambda_m\kappa_m + \sum_{j=1}^{m-1} \frac{(\lambda_j - \lambda_{j+1}q_j)(\kappa_j - \kappa_{j+1}q_j)}{1-q_j^2} \\ \lambda_m\kappa_m + \sum_{j=1}^{m-1} \frac{(\lambda_j - \lambda_{j+1}q_j)(\kappa_j - \kappa_{j+1}q_j)}{1-q_j^2} & \kappa_m^2 + \sum_{j=1}^{m-1} \frac{(\kappa_j - \kappa_{j+1}q_j)^2}{1-q_j^2} \end{bmatrix}, \tag{3.3}$$

where κ_j *is the same quantity as in Theorem 3.1, while* $\lambda_j := -\log(t_j)\exp\big(-B/t_j\big)/t_j^{\mu}$ *if* $t_j \neq 0$*, and* $\lambda_j := 0$*, otherwise.*

Theorems 3.1 and 3.2 show that for estimating merely the trend parameters one can treat the two coordinate directions separately. Hence, in the first coordinate direction the maximum is reached with the equidistant design $d_1 = d_2 = \ldots = d_{n-1}$, while in the second direction one can consider, for instance, the results of Rodríguez-Díaz et al. [27] for the classical OU process.

Example 3.3 Consider a four point grid design, i.e., $n = m = 2$. Without loss of generality we may assume $s_1 = t_1 = 0$ implying $s_2 = d$ and $t_2 = \delta$. In this case the Fisher information (3.2) on B equals

$$M_B(2,2) = \frac{2}{1-\exp(-\alpha d)} \frac{\exp(-2B/\delta)}{\big(1-\exp(-2\beta\delta)\big)\delta^{2(\mu+1)}},$$

which function is monotone increasing in its first variable d. Further, short calculation shows that if $\mu > -1$ then the maximum in δ is attained at the unique solution of the equation

$$\big(B - (\mu+1)\delta\big)\big(\exp(2\beta\delta) - 1\big) = \beta\delta^2.$$

In case $\mu < -1$, that is in particular interesting for chemometricians, one can employ the maximin approach (see, e.g., [16]), which seeks designs maximizing the minimum of the design criterion. In our case this means maximization of

$$\min_{\alpha,\beta>0} M_B(2,2) = 2\exp(-2B\delta)\delta^{-2(\mu+1)}. \tag{3.4}$$

Obviously, if $\mu < -1$ then the maximum of (3.4) is reached at $\delta^* = -(\mu+1)/B$. Although the maximization of (3.4) is pretty easy, one should take care about the interpretation of such a result as, for example, the optimal design does not depend on d.

Maximin approach, anyhow, cannot be automatized without further considerations since, for instance, maximin designs are of no relevance for criteria, where design distances are multiplied by some nuisance parameters, see, e.g., (2.2).

Remark 3.4 Under the conditions of Example 3.3 ($s_1 = t_1 = 0$) we have $\det\big(M_{\mu,B}(2,2)\big) = 0$, that is the four point grid design does not provide information on trend parameters μ and B.

3.2. Estimation of all parameters

Assume first that the rate μ is known and one has to estimate trend parameter B and covariance parameters (α, β). Obviously, the Fisher information matrix on these parameters based on observations $\big\{Y(s_i,t_j),\ i = 1,2,\ldots,n,\ j = 1,2,\ldots,m\big\}$ of the process (3.1) equals

$$\mathcal{M}(n,m) = \begin{bmatrix} M_B(n,m) & 0 \\ 0 & M_r(n,m) \end{bmatrix},$$

where $M_B(n,m)$ and $M_r(n,m)$ are defined by (3.2) and (2.3), respectively. Hence, in order to obtain a D-optimal design one has to maximize $\det\big(\mathcal{M}(n,m)\big) = M_B(n,m)\det\big(M_r(n,m)\big)$.

Example 3.5 Consider again the settings of Example 3.3, that is a four point grid design ($n = m = 2$) under the assumption $s_1 = t_1 = 0$. In this case we have

$$\mathcal{M}(2,2) = \frac{8d^2 \exp(-2B/\delta)\exp(-2\beta\delta)\exp(-2\alpha d)\big(1+\exp(-2\alpha d)+\exp(-2\beta\delta)\big)}{\delta^{2\mu}\big(1-\exp(-2\beta\delta)\big)^3\big(1-\exp(-2\alpha d)\big)^2\big(1+\exp(-\alpha d)\big)}, \qquad d,\delta \geq 0.$$

Tedious calculations show that for $d, \delta \geq 0$ function $\mathcal{M}(2,2)$ is monotone decreasing in d, while in δ it has a maximum at the unique solution of the equation

$$\beta\delta^2 - \mu\delta + B + \mathrm{e}^{2\beta\delta}\big(2\beta(2+p^2)\delta^2 + (B-\mu\delta)p^2\big) + \mathrm{e}^{4\beta\delta}(1+p^2)\big(\beta\delta^2+\mu\delta-B\big) = 0.$$

Hence, the optimal four point grid design collapses in its first coordinate.

If rate μ is also unknown, the Fisher information matrix on (μ, B, α, β) based on $\big\{Y(s_i,t_j),\ i = 1,2,\ldots,n,\ j = 1,2,\ldots,m\big\}$ equals

$$\mathfrak{M}(n,m) = \begin{bmatrix} M_{\mu,B}(n,m) & 0 \\ 0 & M_r(n,m) \end{bmatrix},$$

where $M_{\mu,B}(n,m)$ and $M_r(n,m)$ are defined by (3.3) and (2.3), respectively. In this case the D-optimal design maximizes objective function $\det\big(\mathfrak{M}(n,m)\big) = \det\big(M_{\mu,B}(n,m)\big)\det\big(M_r(n,m)\big)$.

4. Comparisons of designs

Methane emissions compose a very complicated ecological process which contains both stochastic and chaos parts (see, e.g., [2, 28]). Thus, fitting of a two dimensional OU sheet could be a remedy to several problems which occurred in univariate settings [27]. In this section we provide efficiency comparisons for selected important methane kinetic reactions, both in standard (Earth) and non-standard (troposphere) temperature conditions. From this point of view, the current work is the first comprehensive comparison of the statistical information of designs for OU sheets, which gives its novelty both methodologically and from the point of view of applications.

4.1. Comparisons of designs for tropospheric methane measurements

As discussed by Lelieveld [19], tropospheric methane measurements are fundamental for climate change models. Vaghjiani and Ravishankara [32] utilized a 62 point design to measure the tropospheric methane flux. In Theorem 2.1 the exact form of $M_\theta(n,m)$ is derived only for restricted regular designs. One might ask what is the relative efficiency of the optimal value of the Fisher information $M_\theta(n \cdot m)$ on θ based on observations forming monotonic sets of $n \times m$ design points (see [8]), compared to the $M_\theta(n,m)$ of a rectangular grid with the same number of points. Monotonic sets provide natural designs reflecting essential temperature non-reversibility in short time periods. Since the designs for methane used in [32] typically have around 62 points, we should consider a 64 point design comparison of e.g. a 8×8 regular grid with a 64 points monotonic set for covariance parameters $\alpha, \beta \in \{0.001, 0.01, 0.1, 1, 10\}$ and design space

		$\alpha = 0.001,\ \beta = 0.01$	$\alpha = 0.1,\ \beta = 1$	$\alpha = 1,\ \beta = 1$	$\alpha = 1,\ \beta = 10$
$D-opt.$	monotonic	1.3118	29.8651	61.2545	63.9937
	rectangular	1.3328	57.4388	63.7483	64.00
	rel. eff. (%)	98.43	51.99	96.09	99.99
$Ent.$	monotonic	-33.0446	86.1318	90.7964	90.8121
	rectangular	-51.1507	90.7111	90.8119	90.8121
	rel. eff. (%)	64.60	94.95	99.98	100

Table 1: $M_\theta(n,m)$ and entropy values corresponding to the optimal monotonic and to the rectangular grid design and relative efficiency of the optimal monotonic design.

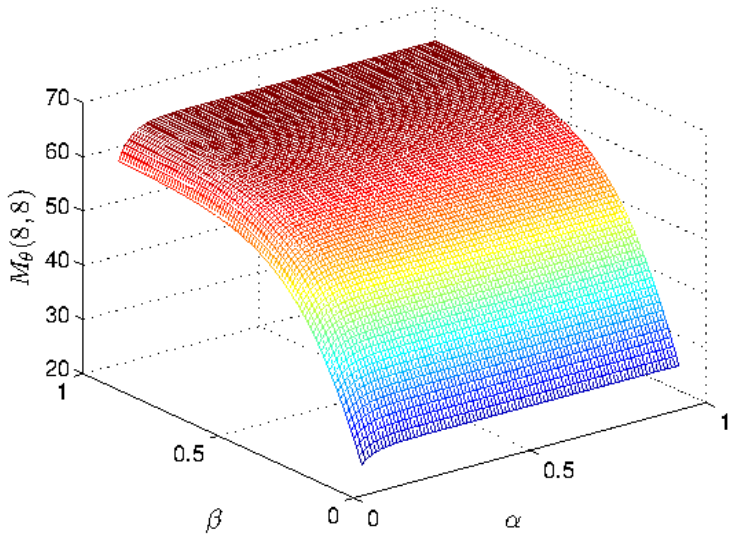

Figure 4: Fisher information on θ as functions of correlation parameters (α, β) for $n = 8$ and $m = 8$.

		$\alpha{=}0.001, \beta{=}0.01$	$\alpha{=}0.1, \beta{=}0.01$	$\alpha{=}0.1, \beta{=}1$	$\alpha{=}1, \beta{=}1$	$\alpha{=}1, \beta{=}10$
$D-opt.$	Bonard et al. [9]	3.1261	8.7785	8.9904	9.0000	9.0000
	mon., $n = 9$	3.2067	8.9107	9.0000	9.0000	9.0000
	3×3 r.grid	3.0305	7.6660	9.0000	9.0000	9.0000
$Ent.$	Bonard et al. [9]	9.8567	12.7665	12.7704	12.7704	12.7704
	mon., $n = 9$	11.2150	12.7703	12.7704	12.7704	12.7704
	3×3 r.grid	9.2225	12.7231	12.7704	12.7704	12.7704
IMSPE	Bonard et al. [9]	6.3624×10^4	1.6246×10^5	1.7220×10^5	1.7231×10^5	1.7231×10^5
	3×3 r.grid	9.3642×10^4	1.6895×10^5	1.7224×10^5	1.7231×10^5	1.7231×10^5

Table 2: $M_\theta(n, m)$ and entropy values corresponding to the optimal monotonic and to the rectangular grid design, IMSPE of the optimal regular grid design, together with values of optimality criteria for measurements given in Bonard et al. [9, Table 1].

$[223, 420] \times [0.84, 43.51]$. Table 1 gives the optimal values of $M_\theta(64)$ on monotonic sets, $M_\theta(8, 8)$ values for regular designs and the relative efficiencies of the optimal $M_\theta(64)$ values on monotonic sets for different combinations of parameters (α, β). Observe, that for $\alpha = 0.1$, $\beta = 1$ the optimal monotonic design gives much lower values of Fisher information on θ than the regular grid, while for the other combinations of parameters the relative efficiency is slightly below 100 %. For the entropy criterion we obtain the same results. In Figure 4 the optimal value of Fisher information on θ is plotted as a function of correlation parameters (α, β) for $n = 8$ and $m = 8$.

4.2. Comparisons of designs for the rate of methane reactions with OH

The growth rate of tropospheric methane is determined by the balance between surface emissions and photo-chemical destruction by the hydroxyl radical OH, the major atmospheric oxidant. Such reaction can happen at various temperature modes, for instance, Bonard et al. [9] measured the rate constants of the reactions of OH radicals with methane in the temperature range $295 - 618K$.

Tables 2–5 provide efficiency of original designs of [9] together with efficiencies of monotonic and regular grid designs 3×3, 2×5, 5×2, 3×4, 4×3, 3×2 and 2×3, respectively. Tables 2–5 utilize the setups

		$\alpha=0.001, \beta=0.01$	$\alpha=0.1, \beta=0.01$	$\alpha=0.1, \beta=1$	$\alpha=1, \beta=1$	$\alpha=1, \beta=10$
$D-opt.$	Bonard et al. [9]	1.1853	6.9087	7.0855	8.7813	9.2477
	mon., $n=10$	1.1858	9.5186	9.7151	10.0000	10.0000
	2×5 r.grid	1.1884	2.0487	6.3460	6.3460	9.9999
	5×2 r.grid	1.1897	5.1192	9.9189	9.9239	10.0000
$Ent.$	Bonard et al. [9]	-0.8169	11.9268	12.5103	14.0660	14.1336
	mon., $n=10$	2.7830	14.1860	14.1882	14.1894	14.1894
	2×5 r.grid	-2.5767	-0.7201	13.8227	13.8227	14.1894
	5×2 r.grid	0.6346	8.2463	14.1892	14.1892	14.1894
IMSPE	Bonard et al. [9]	71.7031	1387	1700.6	1714.8	1742
	2×5 r.grid	174.02	2221	1769	1815.7	1729.6
	5×2 r.grid	67.17	1574.8	1664.2	1724.8	1729.6

Table 3: $M_\theta(n,m)$ and entropy values corresponding to the optimal monotonic and to the rectangular grid design, IMSPE of the optimal regular grid design, together with values of optimality criteria for measurements given in Bonard et al. [9, Table 2].

		$\alpha=0.001, \beta=0.01$	$\alpha=0.1, \beta=0.01$	$\alpha=0.1, \beta=1$	$\alpha=1, \beta=1$	$\alpha=1, \beta=10$
$D-opt.$	Bonard et al. [9]	1.1816	6.7348	6.9218	7.6265	9.0242
	mon., $n=12$	1.1818	10.8570	11.2215	12.0000	12.0000
	3×4 r.grid	1.1850	3.0669	8.6804	8.6804	12.0000
	4×3 r.grid	1.1852	4.0890	10.4462	10.4466	12.0000
$Ent.$	Bonard et al. [9]	-5.7821	3.0845	12.3312	12.9532	16.4642
	mon., $n=12$	1.9060	17.0107	17.0199	17.0273	17.0273
	3×4 r.grid	-4.0505	1.1408	16.7911	16.7911	17.0273
	4×3 r.grid	-2.9378	4.4983	16.9807	16.9807	17.0273
IMSPE	Bonard et al. [9]	61.60	1266.5	1535.5	1599.7	1579.2
	3×4 r.grid	82.20	1710.6	1508.8	1578.9	1540.4
	4×3 r.grid	60.63	1539.7	1471.9	1550.2	1540.7

Table 4: $M_\theta(n,m)$ and entropy values corresponding to the optimal monotonic and to the rectangular grid design, IMSPE of the optimal regular grid design, together with values of optimality criteria for measurements given in Bonard et al. [9, Table 3].

		$\alpha=0.001, \beta=0.01$	$\alpha=0.1, \beta=0.01$	$\alpha=0.1, \beta=1$	$\alpha=1, \beta=1$	$\alpha=1, \beta=10$
$D-opt.$	Bonard et al. [9], $n=7$	1.0057	1.1531	1.5630	2.2240	4.5042
	Bonard et al. [9], $n=6$	1.0057	1.1531	1.5630	2.2240	4.4850
	mon.,$n=7$	1.0057	1.1542	1.5683	2.8570	5.4387
	mon.,$n=6$	1.0057	1.1542	1.5675	2.8309	5.0721
	2×3 r.grid	1.0057	1.1537	1.6244	2.6938	5.6029
	3×2 r.grid	1.0057	1.1545	1.6061	3.1714	4.5396
$Ent.$	Bonard et al. [9], $n=7$	-8.3075	-6.4357	4.9754	5.1821	8.9398
	Bonard et al. [9], $n=6$	-5.4333	-3.5616	5.5473	5.7539	8.3806
	mon., $n=7$	-6.7914	2.9548	6.4778	8.9552	9.8647
	mon., $n=6$	-4.9681	3.1294	6.0021	7.9077	8.4873
	2×3 r.grid	-8.7323	-2.2476	6.1896	7.3797	8.5095
	3×2 r.grid	-9.2498	-0.3290	5.5038	8.1021	8.4115
IMSPE	Bonard et al. [9]	0.006	0.2562	0.5962	2.2074	2.6327
	2×3 r.grid	0.006	0.2538	0.5654	1.9861	2.5682
	3×2 r.grid	0.0083	0.1325	0.7726	1.5183	2.7306

Table 5: $M_\theta(n,m)$ and entropy values corresponding to the optimal monotonic and to the rectangular grid design, IMSPE of the optimal regular grid design, together with values of optimality criteria for measurements given in Bonard et al. [9, Table 4].

described in Tables 1–4 of [9]. These results show that in most of the situations monotonic and regular grid designs outperform the original designs.

Dunlop and Tully [10] measured absolute rate coefficients for the reactions of OH radical with CH_4 (k_1) and perdeuterated methane d_4 (k_2.) Authors characterized k_1 and k_2 over the temperature range $293-800K$.

		$\alpha=0.001, \beta=0.01$	$\alpha=0.1, \beta=0.01$	$\alpha=0.1, \beta=1$	$\alpha=1, \beta=1$	$\alpha=1, \beta=10$
$D-opt.$	Dunlop and Tully [10]	4.5728	9.4857	9.9959	10.0000	10.0000
	mon., $n=10$	4.7604	9.9721	10.0000	10.0000	10.0000
	2×5 r.grid	4.9144	7.8743	10.0000	10.0000	10.0000
	5×2 r.grid	2.5049	9.9944	9.9999	10.0000	10.0000
$Ent.$	Dunlop and Tully [10]	12.2328	14.1366	14.1894	14.1894	14.1894
	mon., $n=10$	13.3584	14.1894	14.1894	14.1894	14.1894
	2×5 r.grid	12.9678	14.0944	14.1894	14.1894	14.1894
	5×2 r.grid	8.2035	14.1894	14.1894	14.1894	14.1894
IMSPE	Dunlop and Tully [10]	1.9903×10^5	4.0788×10^5	4.1836×10^5	4.1848×10^5	4.1849×10^5
	2×5 r.grid	2.3148×10^5	4.2273×10^5	4.1842×10^5	4.1848×10^5	4.1849×10^5
	5×2 r.grid	4.2333×10^5	4.1171×10^5	4.1842×10^5	4.1848×10^5	4.1849×10^5

Table 6: $M_\theta(n, m)$ and entropy values corresponding to the optimal monotonic and to the rectangular grid design, IMSPE of the optimal regular grid design, together with values of optimality criteria for k_1 measurements given in Dunlop and Tully [10, Table 1].

		$\alpha=0.001, \beta=0.01$	$\alpha=0.1, \beta=0.01$	$\alpha=0.1, \beta=1$	$\alpha=1, \beta=1$	$\alpha=1, \beta=10$
$D-opt.$	Dunlop and Tully [10]	3.0778	11.7720	11.9798	12.0000	12.0000
	mon., $n=12$	3.1465	11.8465	12.0000	12.0000	12.0000
	3×4 r.grid	3.3749	8.0858	12.0000	12.0000	12.0000
	4×3 r.grid	3.1184	9.9557	12.0000	12.0000	12.0000
$Ent.$	Dunlop and Tully [10]	11.2608	17.0260	17.0272	17.0273	17.0273
	mon., $n=12$	13.7036	17.0270	17.0273	17.0273	17.0273
	3×4 r.grid	12.9774	16.6656	17.0273	17.0273	17.0273
	4×3 r.grid	11.3202	16.9405	17.0273	17.0273	17.0273
IMSPE	Dunlop and Tully [10]	1.9924×10^5	1.9924×10^5	2.1087×10^5	2.1099×10^5	2.1100×10^5
	3×4 r.grid	8.6341×10^4	2.1154×10^5	2.1097×10^5	2.1100×10^5	2.1101×10^5
	4×3 r.grid	1.1094×10^5	2.0596×10^5	2.1091×10^5	2.1100×10^5	2.1101×10^5

Table 7: $M_\theta(n, m)$ and entropy values corresponding to the optimal monotonic and to the rectangular grid design, IMSPE of the optimal regular grid design, together with values of optimality criterion for k_2 measurements given in Dunlop and Tully [10, Table 2].

Finally, they found an excellent agreement of their results with determinations of k_1 at lower temperatures of [32]. Now, let us consider rates k_1 and k_2 of Table 1 of [10]. We obtain the following comparisons (Table 6–7) of efficiencies of the monotonic and 2×5 and 5×2 regular grid designs with the original designs of [10]. As we can see, in most of the cases, the monotonic and regular grid designs are more efficient than the original one. This is in line with the fact that monotonic designs are natural for modelling temperature non-reversibility in short time intervals. Several implementations of Latin Hypercube designs can be an alternative to regular grid designs, however, they do not reflect non-reversibility of chemical processes and for small design sizes are outperformed by monotonic grid designs (see [8]).

5. Conclusions

Both Kyoto protocol [19] and recent Scandinavian and Polish summits in 2013 pointed out necessity to develop precise statistical modelling of climate change. This, in particular should be addressed by developing of optimal, or at least benchmarking designs for complex climatic models. The current work aims to contribute here for the case of methane modelling in troposphere, lowest part of atmosphere. As can be well seen in the paper, optimal designs for univariate case (OU process, see [27]) and planar OU sheets differ. Obviously, planar OU sheet is much more precise, since it allows variability both in temperature (main chemically understood driver of chemical kinetics) and in a second variable, which can be either atmospheric pressure or any other relevant quantity. Temperature itself is also regressor, i.e., variable entering into trend parameter k_1. One valuable further research direction, enabled by the second variable "s" will be direct modelling of reaction kinetics. The optimal design for spatial process of methane flux can be helpful for

better understanding the emerging issues of paleoclimatology [22], which in major part relates to large variability.

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