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The future of computational modelling in reaction engineering

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Abstract

In this paper we outline the future of modelling in reaction engineering. Specifically, we use the example of particulate emission formation in internal combustion engines to not only demonstrate what modelling can achieve at present but more importantly to illustrate the ultimately inevitable steps which need to be taken in order to create a new generation of engineering models.

Contents

1 Introduction

The use of computational modelling in engineering has gained increasing momentum over the last three decades. The main cause for this has been the massive advance in computer power. Industry is making use of computational models to increase the speed of technical development, which is an important factor in the overall competitiveness of a company. Environmental considerations, such as global warming and pollution reduction demand constant development of new products for an ever changing set of constraints defined by the market and government. It is clear that computational modelling will play an increasingly significant role in this optimisation process as it reduces the cost of development. Here, we will focus on the use computational models describing particulate formation in an internal combustion engine (ICE). This choice is exemplary for many problems in reaction engineering and the problems and solutions described in the following are relevant to many fields of engineering. Although there has been a great deal of progress in applying computational methods to engineering problems there are some important difficulties with the current approach which prevent further progress.

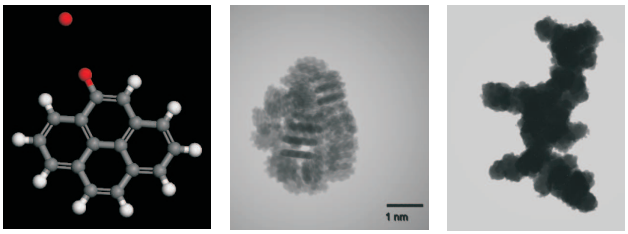
The **purpose of this article** is to discuss how computational modelling is evolving in the near and not so near future. Starting with the present we describe the state of the art of modelling soot formation in ICEs across multiple length scales. Using this example we discuss the limitation of this approach by defining what a model is on a more formal level. We proceed to show how statistics, standardisation of data and models, data collaboration over the world wide web, and the automation of experiments will lead to a new generation of more robust models. We argue that these developments will eventually lead to robot engineers which support model building.

2 Modelling across multiple length scales

In this section, we show how multiscale modelling has been implemented for ICEs and also suggest improvements. One can separate the problem into the micro or molecular, meso or nanoparticle, and macro or continuum scale.

Complex reaction networks. Gas phase combustion chemistry can be investigated using detailed chemical models sometimes called mechanisms. These mechanisms are collections of species and reactions, *i.e.* detailed descriptions on the molecular level. Such a model for a fuel can contain up to several thousand reactions whose rates are given by the so called Arrhenius expression containing at least three constants. There are two major difficulties with this approach. Firstly, the determination of the rate constants and secondly, despite the size of the models, there may still be a number of important pathways missing. The latter problem can be addressed by generating the reaction networks automatically and simultaneously reducing them [6].

Quantum chemistry and statistical mechanics. The reaction rate constants can be obtained from either parameter fitting to specially designed experiments, or directly from quantum calculations. Using results from these calculations, rate constants and thermodynamical properties of molecules can be calculated using statistical mechanics and



(a) *PAH molecule.* **(b)** *PAH cluster.* **(c)** *Soot aggregate.*

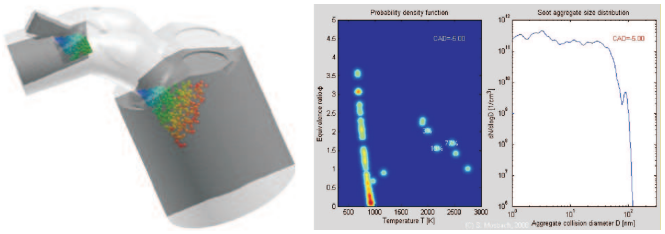
Figure 1: *Multiscale modelling - micro and meso scale.*

(variational) transition state theory. A number of software packages are available offering various degrees of accuracy and functionality. The most popular ones are based on density functional theory (DFT) and can be used to calculate the geometry and electronic energy of a molecule. Transition states can be calculated from the same packages by searching for saddle points on the potential energy surface. Figure 1(a) shows a transition state of an oxygen molecule reacting with a PAH molecule [3].

Molecular dynamics and kinetic Monte Carlo. For larger molecules and clusters of molecules quantum calculations become unfeasible. Instead, molecular potentials can be fitted to the potential energy surfaces of individual atoms. The most commonly used of these is the Lennard-Jones potential. These potentials can then be used in a various ways, often providing excellent approximations to electronic structure calculations. Figure 1(b) shows the result of a basin hopping algorithm with which an energetically favourable structure of 50 coronene molecules has been calculated [15]. Particles of this size play an important role in the formation of soot. The dynamics of small molecular clusters can be described using molecular dynamics (MD) techniques, where the equations of motions are solved directly. For large clusters coarse graining of the molecular potentials is necessary. The chemical growth of large molecules or particles, *i.e* the chemical reactions with the surrounding gas, can be modelled with a Kinetic Monte Carlo (KMC) simulation [11].

Population balance. The dynamics of the particle population is modelled on a meso scale using a multivariate population balance equation which is coupled to the gas phase chemistry. In the past, each particle used to be described simply by mass and surface area. However, progress in the numerical treatment of population balance equations made it possible to extend this description considerably to include a large number of internal variables such as the chemical composition and the spatial structure of an aggregate [2]. Figure 1(c) shows a soot aggregate as an example.

Fluid dynamics. Transport of the gas and particulate phase on the macro level is determined by conservation equations for all chemical components, momentum, and energy. In an ICE the flow is non-stationary and turbulent, and the geometries are complex which means a direct numerical simulation of the problem is currently not practical. Computational Fluid Dynamics (CFD) software packages employ a variety of turbulence models which can be solved for a complex geometry. A major challenge is that in modern engines fuel is injected into the engine cylinder in liquid form as spray. This process is only poorly understood which means that all spray models have strong empirical components



(a) *Spray in an ICE.* **(b)** *Soot PSD in a DISI engine.*

Figure 2: *Multiscale modelling - macro scale.*

and require fitting to the specific conditions which are to be modelled. Figure 2(a) shows a CFD simulation of a spray injection in a PCCI engine [1].

Reaction engineering models. Presently it is not possible to include detailed fuel and particle models into CFD simulations without making significant simplifications. For this reason classical models from reaction engineering are combined with CFD. These models make some gross simplifying assumptions on spatial resolution which render the corresponding mathematical equations numerically tractable. Multi-zone models as well as stochastic reactor models (SRMs) have been widely used, for example [10] used an SRM with a detailed chemistry and soot model. Figure 2(b) shows the result of a stochastic reactor model which includes a detailed chemistry model for a real fuel coupled to a detailed model for soot particles to predict emissions in a direct injection spark ignition engine. The boundary conditions for SRMs can be obtained from CFD simulations.

3 General description of a model

The previous section illustrated how a variety of models on different scales can be combined into one model for an internal combustion engine. One important purpose of a model in engineering is to inform a user about the properties of an industrial application and to make some forecasts about the system based on how the model behaves when certain settings are changed. Ultimately, this can be used to improve upon the current design or settings. Although multiscale modelling has been a partial success there are a number of open problems. In order to analyse these problems, it is helpful to formalize the notion of a model.

Characterization of a (multiscale) model. The schematic in Figure 3 shows important elements of a comprehensive multiscale model, which is called model k to indicate that it can be considered part of a sequence of models in which each model aims to improve upon its predecessor. The model itself is comprised of application models (AMs), instrumental models (IMs), and data models (DMs) together with a choice of parameter estimation methodology and numerical methods. An application model is directly inspired by the physics underlying the phenomenon we are interested in. For example, application model one, AM(i_1), concerns one of the molecules in the chemical mechanism, AM(i_2) describes the fuel chemistry as a whole, AM(i_3) describes soot particle inception, AM(i_4) describes the heat transfer, and so on. Application models may be nested in other ap-

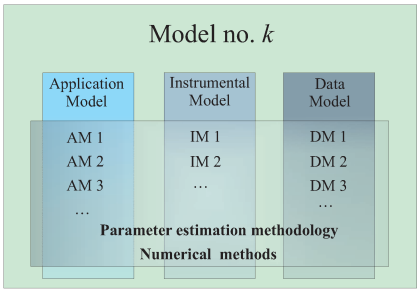


Figure 3: *Schematic of a model.*

plication models each containing a set of parameters. As the parameters are not known exactly it is necessary to specify an uncertainty for each parameter. This can either be a deterministic range, an interval in which the parameter must lie, or a probability density. Each application model is formulated in terms of mathematical equations, mainly ordinary or partial differential equations but also stochastic processes, as in the case of an SRM or the population balance equation. The numerical method for each application model also needs to be specified including the chosen numerical parameters. Application models need validation and for this reason they are fitted to experimental data. In the case of an ICE various experimental configurations are used for validation, engine tests for validating the final engine model, laminar flame and shock tube studies for validating the chemistry submodels, *etc.* A typical quantity of interest in a flame experiment is the concentration of a chemical species. Using laser techniques fluorescence signals are measured. This data is described by a data model which specifies the raw data, the systematic error associated with the measurement and the experimental apparatus and settings. From the raw data the information of interest is then derived using an instrumental model. For example, a light intensity obtained from an extinction measurement is used to calculate soot volume fraction from Mie theory using assumptions on the refractive index of soot particles. The instrumental models, as the application models, are based on physical insight and formulated in terms of mathematical equations. The model k is finally specified by the mathematical fitting techniques and the objective function which are used to specify parameters of the application models by minimizing the objective function, *i.e.* the "difference" between application and instrumental models.

Problems with the present approach. Ideally, when one moves from model k to model $k+1$ one expects an improvement in predictive power. At present this is unfortunately not guaranteed partly because the improvement cannot be measured. The lack of predictive power is mainly caused by incomplete information and non-systematic model building. As pointed out earlier the number of parameters largely exceeds the number of experimental data available for validation. This means that the model can almost always be fitted to experimental results. Therefore falsification of model assumptions and true model development is not possible. In the literature raw data is almost never published, which means that the instrumental model and the data model cannot be separated and conflicting assumptions in application and instrumental model may exist. Also, the instrumental model is often not fully specified, which makes comparison between application model and derived experimental data impossible. Detailed description of the experimental setup to the extent that the initial and boundary conditions for the application models

can be fully specified is often missing in journal articles. The lack of error propagation constitutes another common problem. This problem occurs because errors in raw data are not propagated through to the instrumental model and not incorporated into the objective function which is used to fit application models to instrumental models. Even when experiments and application models are specified the numerical treatment of the mathematical equations is often unsatisfactory. In the engineering community there are many examples where the numerical method is intermingled with the model formulation, which makes reproduction of the results very difficult.

How can these problems be solved? In the next three sections, we shall introduce techniques which are necessary to alleviate some of these problems. The world wide web, modern statistics, automated experiments, and most of all massive computing power will play a key role.

4 The role of statistics

Statistics and operational research offer a number of concepts which are useful in model formulation, improvement, and selection. In statistics both the frequentist and the Bayesian approach can be adopted. In Bayesian statistics the parameters are viewed as random variables.

Model reduction. As described earlier the model is normally very complex and requires numerical solution which may render a statistical approach prohibitive because of limits in CPU time available. Moreover the number of parameters is normally very high. In combustion models there are frequently more than 1000 parameters. For both of these reasons model reduction is almost always required. There are many techniques with which such a reduction can be achieved. In particular, reducing the chemical submodel is necessary. Sensitivity and flux analysis are just two techniques which have been applied in the past.

Approximation of model response. Even a reduced model is often too computationally expensive to be used in optimization algorithms, for example, as part of a parameter estimation technique. For this reason the model response has been approximated by either a tabulation procedure or a locally fitted response surface, also called response surface methodology (RSM). [9] have developed a tabulation method for an engine model which makes use of cubic natural splines. This technique is suitable if the number of unknown parameters is relatively low, typically less than five. For larger number of parameters the RSM can be combined with Latin Hypercube sampling or low discrepancy sequences to obtain an approximated model response in hypercubical subdivisions of the parameter space. In chemical engineering applications linear models have been used to construct response surfaces [4].

Parameter estimation. In the frequentist approach one assumes that the model response is distributed according to a known probability distribution with unknown parameters. For a given set of experimental data, which are also assumed to be realizations of random variables, representing statistical and systematic error in the measurement, optimization yields new estimates for the parameters. In the Bayesian framework the parame-

ters themselves are random variables. Starting from a prior distribution of the unknown parameter, which can incorporate any additional knowledge, Markov chain Monte Carlo (MCMC) can be used to obtain empirical posterior densities of the model parameters. This posterior can then be further analyzed. For example, using kernel marginalization, one can calculate credible regions such as the highest probability density (HPD) regions for parameters and model responses. For a combustion problem a somewhat similar approach has been successfully used in conjunction with model reduction by [13]. An alternative, deterministic approach has been developed by Frenklach and coworkers [4]. Based on a set of experimental data and a general nonlinear model the concept of data consistency is formulated by considering bounds on the model prediction error and the a-priori bounds on the parameters. If there is a mismatch in these two regions, then the data is considered inconsistent. The consistency measure developed relies on a complex optimisation in which branch and bound and trust region techniques are employed. Lagrange multipliers computed in the optimisation are used to consider the sensitivity of the consistency measure with respect to the a-priori assumptions on the parameter and data error bounds.

Design of experiments. All the above approaches can be used to suggest new experiments to reduce the uncertainty in the model parameters and therefore increase the predictive power of a model. In the classical frequentist experimental design a new design can be found, for example, by maximizing the Fisher information matrix, which is a measure how much information one has about the unknown parameters. Different designs are obtained by using different maximization criteria, for example, D-optimality maximizes the determinant of the Fisher information matrix, i.e. it minimizes the volume of the ellipsoid confidence regions for the unknown parameters. Similarly, Frenklach and coworkers determine the sensitivity of uncertainties in model predictions with respect to uncertainties in the underlying experimental data. Thus providing suggestions as to which, if refined, measurement would result in significant uncertainty reduction. In addition, Lagrange multiplier methods can be employed to calculate the sensitivity of dataset consistencies with respect to other experimental results and *a priori* information [4], thereby enabling identification of data entries which most inhibit the consistency of a dataset. In the Bayesian framework an experimental design can be obtained by maximizing an utility function with respect to all experimental designs. However, the computation of the optimal experimental design requires the maximization of two nested integrals which can be computationally very expensive.

Model discrimination. All of the above approaches can be used for model discrimination. The aim is to falsify a model based on a set of experimental data. For example, [8] have extended the approach by [13] to resolve conflicting parameter estimates in multivariate population balance models.

5 The role of the world wide web

Incomplete information. In the past, experimental data has been taken from the literature, which means that data were extracted manually from published articles. This has a number of disadvantages which crucially influence the quality of a model. The foremost problem is that the information available to the model builder is incomplete. So far, ex-

perimentalists have almost always reported data which has been derived from raw data. The instrumental models used as well as the assumptions made in these models are, if at all, only implicitly stated. Furthermore, uncertainties associated with the raw data and detailed error propagation analysis of the instrumental model are often missing. A further problem is that the experimental set-up is not described in enough detail to fully specify initial and boundary conditions necessary to find a numerical solution of the model. This situation is improving as many scientific journals now include additional information on the web along with the electronic version of the corresponding article. However, this information is often in proprietary or software specific standards and therefore requires access to specific software tools which in many cases are not available as open source. But even if this information is provided a researcher may not have access to expensive journals in which the experimental data including supplementary data has been published. While this can be circumvented by contacting the author directly in many cases, PhD students who carried out the experimental work may not have stored the raw data of their experiments and their laboratory log books may not be available.

Metadata for models. In order to overcome these problems the following issues need to be addressed: standardization, accessibility, and automation. Computer science has developed a number of concepts which may be used to progress on these issues. Ideas based on the "Semantic Web" seem to be particularly promising and have already been adopted by the science and engineering community. The World Wide Web Consortium (W3C), an organisation which defines web standards such as HTML, XML, RDF, SPARQL, *etc.* has envisioned the Semantic Web as a web of data that enables computers to process and **understand** information on the web.

Extensible Markup Language (XML) aims to provide new standards for encoding documents and organizing their contents over the Internet. XML allows the flexible development of user-defined document types. It provides a core set of standards developers can use to create their own. For this reason XML is suitable to provide a framework for specific standards of data and models that occur in the engineering community. As XML is becoming a global standard, parser libraries are available in a large number of programming languages, *e.g.* FORTRAN, C, C++, Java, Python, *etc.* This allows data to be exchanged between different software packages regardless of programming language. In the combustion community, first applications of XML data representation have emerged. The PrIMe Data Model (PDM, [5]) is a proposed standard based on XML technology, which aims to standardize many aspects related to modelling combustion chemistry using detailed chemical kinetics. The Computational Modelling Group has developed an XML specification for internal combustion engine data called EngineML [14]. All these XML representations have in common that each piece of data must comply with an "XML schema" which specifies the data model and acts as a grammar for the XML data sets. Validation tools exist which can be used to check whether a specific piece of data is consistent with a given standard.

Although XML is suitable to represent standardized data it does not explicitly relate data entries to each other. In order to query the XML data the data has to be processed by specific software. To use XML data sets in any application, one needs to understand the particular XML representation. In the "Web data" as described by W3C, the web resources are well described by its relationship to one another. In the Semantic Web this

issue can be addressed through RDF (Resource Description Framework). RDF uses the concept of "Entity-Relationship" based on the idea of making a statement about the data and their relations so the web data is not only human-understandable but also machine-understandable. RDF formalizes the free-form hierarchical structures of XML into triplets of subject, relationship, and object. Thus, in order to obtain a piece of information, a search query can be performed by traversing the graph formed by the collection of triplets, using an RDF query language such as SPARQL. The open source software openRDF provides a framework for storing, inferring, and querying of RDF data allowing a human user to work with the RDF repository. Work is in progress to extend the use of RDF beyond EngineRDF to the PrIMe data models as well as to output of the quantum chemistry package Gaussian (QuantumML and QuantumRDF). Although a XML and RDF schema check the consistency of data they do not check whether or not the relations contained in RDF are meaningful and consistent. To address this problem the W3C has introduced OWL (Web Ontology Language), a language which is built upon RDF and RDF Schemas. It is designed to rigorously define the description of things and their relationships. The web ontology also provides the ability to validate RDF documents beyond schema validation. Ontologies for EngineRDF and QuantumRDF are under development. The ultimate aim is to create ModelML and ModelRDF which represent the full model k as described in the previous sections.

6 Synthesis: automatic experimentation

In the previous section experimental design was discussed based on a hierarchy of detailed physical models. The natural progression is for these experiments to be conducted automatically. In biology this has already been achieved when "Adam", the first robot scientist, was created by [7]. Adam can conduct high-throughput individually designed microbial batch growth experiments measuring growth curves (phenotypes) of selected microbial strains (genotypes) growing in defined media (environments). However, the experimental design is a data driven approach and does not use scientific knowledge in the form of physical or chemical models. In chemical engineering, automation of experiments is commonplace from bench to industrial scale. For example, in Cambridge a tank reactor has been automated using the industrial plant scale Siemens PCS7 system to control a chemical reaction [12]. In this experiment, user and engineering interface is completely accessible over the internet. Using a computer to provide the necessary input of initial and boundary conditions for the experiment represents no extra technical hurdle.

A full representation of the model k in XML as outlined above allows model improvement to be fully computer driven. Sensitivity analysis will indicate which application models are important with respect to the variables of interest. The computer can design experiments to produce additional data to reduce the variance in the important parameters using, for example, Bayesian techniques. If the experiment is set up, this step can be fully automated, *i.e.* a robot can carry out the experiments. Adam generates knowledge in functional genomics using scientific reasoning allowing it to form hypotheses, design experiments to test these, and finally to carry out the experiments. The approach outlined in this paper differs in that the models used by the computer include physical insight as

opposed to being entirely data driven. This is because the computer can set up quantum calculations to calculate properties of chemical species and reactions and employ conservation equations to calculate what happens on an industrial scale. This new system will be connected to the internet giving it access to a plethora of web applications. Using Semantic Web technology it will be able to take advantage of the latest experimental results from around the globe. It could conceivably even have access to real time industrial operating conditions and results. This methodology will lead to a step change in the relationship between scientists, engineers, and business professionals. Real economic decisions can be made by companies on the basis of reliable, comprehensive, and cheap models.

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References

[1] L. Cao, A. Bhave, S. Mosbach, H. Su, M. Kraft, A. Dris, and R. M. McDavid. Influence of injection timing and piston bowl geometry on PCCI combustion and emissions. *SAE Paper No.* 2009-01-1102, 2009.

[2] M. Celnik, R. Patterson, M. Kraft, and W. Wagner. A predictorcorrector algorithm for the coupling of stiff ODEs to a particle population balance. *Journal of Computational Physics*, 228(8):2758–2769, 2009. doi:10.1016/j.jcp.2008.12.030.

[3] M. S. Celnik, M. Sander, A. Raj, R. H. West, and M. Kraft. Modelling soot formation in a premixed flame using an aromatic-site soot model and an improved oxidation rate. *Proceedings of the Combustion Institute*, 32, 2009. in press.

[4] R. Feeley, P. Seiler, A. Packard, and M. Frenklach. Consistency of a reaction dataset. *The Journal of Physical Chemistry A*, 108:9573–9583, 2004. doi:10.1021/jp047524w.

[5] M. Frenklach. Transforming data into knowledge – process informatics for combustion chemistry. *Proceedings of the Combustion Institute*, 31:125–140, 2007. doi:10.1016/j.proci.2006.08.121.

[6] W. H. Green. Predictive kinetics: A new approach for the 21st century. *Advances in Chemical Engineering*, 32:2–50, 2007. doi:10.1016/S0065-2377(07)32001-2.

[7] R. D. King, J. Rowland, S. G. Oliver, M. Young, W. Aubrey, E. Byrne, M. Liakata, M. Markham, P. Pir, L. N. Soldatova, A. Sparkes, K. E. Whelan, and A. Clare. The automation of science. *Science*, 234(5923):85–89, April 2009.

[8] P. Man, A. Braumann, and M. Kraft. Resolving conflicting parameter estimates in multivariate population balance models, 2009. Technical Report 82, c4e-Preprint Series. Submitted to *Chemical Engineering Science*.

[9] S. Mosbach, A. M. Aldawood, and M. Kraft. Real-time evaluation of a detailed chemistry HCCI engine model using a tabulation technique. *Combustion Science and Technology*, 180(7):1263–1277, 2008. doi:10.1080/00102200802049414.

[10] S. Mosbach, M. S. Celnik, A. Raj, M. Kraft, H. R. Zhang, S. Kubo, and K.-O. Kim. Towards a detailed soot model for internal combustion engines. *Combustion and Flame*, 156(6):1156–1165, 2009. doi:10.1016/j.combustflame.2009.01.003.

[11] A. Raj, M. Celnik, R. Shirley, M. Sander, R. Patterson, R. West, and M. Kraft. A statistical approach to develop a detailed soot growth model using PAH characteristics. *Combustion and Flame*, 156(4):896–913, 2009. ISSN 0010-2180. doi:10.1016/j.combustflame.2009.01.005.

[12] A. Selmer, M. Kraft, R. Moros, and C. K. Colton. Weblabs in chemical engineering education. *Education for Chemical Engineers*, 2:38–45, 2007.

[13] D. A. Sheen, X. You, H. Wang, and T. Løvås. Spectral uncertainty quantification, propagation and optimization of a detailed kinetic model for ethylene combustion. *Proceedings of the Combustion Institute*, 32(1):535–542, 2009. doi:10.1016/j.proci.2008.05.042.

[14] A. Smallbone, A. Bhave, S. Mosbach, W. Phadungsukanan, A. Braumann, M. Kraft, A. Dris, and R. M. David. Using process informatics to achieve more rapid and systematic experimental/model developments for IC engines. *JSAE Paper No.* 134-20095490, 2009.

[15] T. Totton, D. Chakrabarti, A. Misquitta, M. Sander, D. Wales, and M. Kraft. Modelling the internal structure of nascent soot particles. *Combustion and Flame*, in press, 2009.