

Finite Rate Chemistry

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Chemical and nuclear reactive flows are important to DOE science. Major uncertainties and errors in simulations for these problems derive from three sources. First, is the uncertainty or errors in the reactions and the reaction rates. Second is the use of models (flame structure models) to describe the internal dynamics of the flame front, often based on a quasi-equilibrium, slow manifold assumption, or a sharp flame front approximation and thirdly, the numerical errors and uncertainties in the underlying hydro simulation which supports the reaction process. Finite rate chemistry describes a numerical effort to completely avoid the second issue, through resolution of the internal flame structure, with chemistry based on local reaction rate laws (Arrhenius kinetics). Here we describe mathematical developments needed to achieve finite rate chemistry at the exascale.

Chemistry is notorious in being very stiff, meaning that there are a number of fast reactions, needing small time steps and high spatial resolution for pure finite rate chemistry to work. In practice, with the proliferation in the number of intermediate species and radicals (some 90 are used for a complete description of the burning of methane), and with many rates not well characterized experimentally or through quantum simulations, a reduced combustion model will be required. This is the first issue mentioned above, and is not the topic of this white paper. The third issue, of numerical convergence of the hydro aspects of the simulation, will no doubt succeed at the exascale level and usually does not even need this, with petascale Large Eddy Simulations (LES) sufficient in many cases.

The second above issue, to replace flame models with finite rate chemistry, will not be resolved by exascale computing alone. Advances in theoretical and applied mathematics (or chemistry/physics) are also essential. Finite rate chemistry is (in part, but only in part) an exascale issue. The numerical resolution needed for this method is not at the commonly asserted direct numerical simulation (DNS) level, but the less demanding and often attained level of mesh resolution of the flame structure, including its internal layers. DNS of full blown engineering problems will not be attained at the exascale level, but highly resolved LES simulations, sufficient to support stochastic convergence, certainly will be.

To achieve converged LES for reacting flows, it is necessary to address the subgrid fluctuations, in that chemical and nuclear reactions progress only when individual atoms are colliding, and even then they depend on the energy (derived from the temperature) of the collision. Thus we see that convergence of stochastic phenomena is required. Here exascale will play an enabling role. The mesh resolution needed to achieve deterministic convergence (convergence of mean quantities or even of variances of fluctuations) is typically far less than the DNS level of resolution to eliminate these fluctuations at the grid level. We estimate that stochastic convergence is also far less expensive than DNS convergence, and also feasible for the exascale. We estimate that many full blown engineering problems will be amenable to finite rate chemistry supported by stochastic convergence, with the use of exascale computing.

Now we come to the applied mathematics issue. Stochastic convergence is a largely open issue, especially as will be required in the context outlined above. We refer to convergence of probability

density functions (pdfs) or their first integral, the cumulative distribution functions (cdfs). A minor miracle occurs. If the pdfs/cdfs converge, so do the nonlinear functionals of the solution. Thus the reaction rates of Arrhenius chemistry, with their exponential dependence on temperature and their power law dependence on concentrations, converge. With the internal structure of the flame resolved, an exascale feasible goal, the chemistry converges, and reaction models (the second issue, and the main objective of this white paper) are no longer needed.

We have developed the beginnings of an applied mathematics theory of stochastic convergence, suitable to support finite rate chemistry of reacting flow problems.

We have observed the sensitivity and nonuniqueness of LES for reactive or even passive mixture problems, due to the inconsistent treatment of the subgrid scale (SGS) terms [MelRaoKau13, MelRao13a]. Through validation with laboratory experiment, we have found that a commonly used SGS model, the dynamic SGS, [MoiSquCab91] in combination with our simulation codes, achieves consistent agreement with numerous turbulent mixing experiments [LimIweGli10, IweLimGli10a, GliShaKam13], and we have formulated a plan [MelRao13a] to extrapolate this result to high or infinite Reynolds (Re) numbers, with simulation (i.e., verification) based control over the errors. The influence of the perturbation from experimental to infinite Re appears to be small, considered at a hydro simulation level.

Convergence in an L_1 norm of the cdfs has been observed [MelRaoGli13], as well as their sensitivity to modifications of the SGS models. Thus the SGS models are an important issue, a matter we have studied through an analysis based on the renormalization group (RNG) [LimKamYu12, GliPloSha13], but the SGS expansion terms so identified fail to be positive definite, and further modification is needed to exploit this circle of ideas. Using these ideas, we expect that the infinite Re limit is not unique. Numerical convergence of the cdfs requires a novel notion of convergence, which is akin to the mathematical notion of Young measures and w^* convergence [KauGliSha10a, KamKauGli11, KamLimYu11, KamMelRao13, KauKamYu12, LimKamYu12]. In this newly formulated notion of convergence, a single mesh based solution is coarsened onto a coarse mesh, not through averaging, but through binning of the coarse block (supercell) set of values to define an approximate pdf/cdf located in the supercell. Various tradeoffs in the setting of the parameters for w^* convergence have been examined [MelRaoKau13, MelRaoKau13a].

This very weak notion of convergence appears to capture the reality of LES convergence on feasible meshes, probably including exascale LES meshes for full scale engineering problems. For mathematical convergence, we should expect more traditional notions of convergence, depending on the objects selected for convergence. To explore this question, we assumed Kolmogorov type velocity statistics and on this basis proved convergence of the velocity field to an L_p solution of the Euler equations for some value of p [CheGli12] in the limit of infinite Re.

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