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Sandia-Stanford collaboration demonstrates two-line PLIF engine diagnostic

For the past several years, the CRF engines group has been collaborating with Ron Hanson's research group at Stanford University for the development and application of optical diagnostics optimized for internal combustion engines. Sandia benefits from the university's experience in the area of fundamental photophysics, and Stanford gains the opportunity to apply new diagnostics in the CRF's stable of optical engines. Recently, two Stanford graduate students, Dave Rothamer

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Combustion study may impact chemistry of vision

The vinyl radical (C_2H_3) is an important reactive intermediate in combustion chemistry that may play a role in molecular weight growth chemistry leading to the production of soot. A clean source of vinyl radicals is essential for the study of vinyl radical reactions. Recently, a group of researchers at the CRF found that vinyl iodide (C_2H_3I), the heaviest member of the vinyl halide family, can be a clean source of vinyl radicals. This research unexpectedly gave rise to a new understanding of the trends in photodissociation pathways of vinyl halides that could make an impact on our understanding of the primary photochemical processes in vision.

Vinyl halides, having the general formula C_2H_3X (X = F, Cl, Br, I), are substituted forms of ethylene (C_2H_4) and have been used as simple models for the cis/trans photo-induced isomerization of the protein retinal, the key component in human vision chemistry. Until this work, little was known of the photochemistry of the heaviest vinyl halide, C_2H_3I. A team of CRF scientists led by David Osborn discovered that vinyl iodide has remarkably different photochemistry from all the lighter halides, and does not undergo cis/trans isomerization upon excitation with ultraviolet (UV) light.

Upon absorbing a UV photon, vinyl halides can decay via the following channels:

$$C_2H_3X \rightarrow C_2H_3 + X \quad \text{(atomic channel)} \quad (1)$$

$$\rightarrow HCCH + HX \quad \text{(molecular channel)} \quad (2)$$

The product channel producing an atom (1) occurs primarily on excited electronic states, whereas the molecular channel (2) takes place after the excited vinyl halide returns to the ground electronic state, often undergoing a cis/trans isomerization in the process. Previous measurements have shown that after ultraviolet excitation, C_2H_3F decays only via the molecular channel, whereas C_2H_3Cl and C_2H_3Br decay to channels (1) and (2) with about a 1:1 ratio. The CRF team found that C_2H_3I decays only via the atomic channel, making it a clean source for vinyl radicals in combustion studies.

This observation raises the question of why such a marked change in photodissociation dynamics occurs as the halogen atom is changed from F → I. Research on vinyl halide electron energy loss spectra from the University of British Columbia, combined with electronic structure calculations from the CRF, have revealed the answer.

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Conjectured turbulent-burning-velocity law proven mathematically

One of the most basic, yet technologically important questions one can ask about combustion processes is how fast burning occurs. In reacting flows, the rate of burning is affected both by the flame speed at each location on the flame front and by the total flame front area. In a uniform fuel-air mixture, the local flame speed depends on both the chemical state and flame front geometry, which influence the transport of heat into the unburned mixture. The flow modifies front geometry and thus flame speed, and also modifies (and in general increases) the total flame front area, thus affecting the overall burning rate in two different ways. Additional complications include flow effects not directly linked to front geometry and effects of thermal expansion on the flow field.

Thus, it is not surprising that the dependencies of the overall burning rate of a uniform mixture on fuel chemistry and on combustor geometry (which affects the flow) are significant and complicated. Successfully creating predictive models of combustion processes requires a greater understanding of these dependencies.

Jackson Mayo, a postdoctoral associate working with CRF researcher Alan Kerstein, has performed a mathematical and computational study that is a step toward achieving the necessary insights. Central to the analysis is consideration of the turbulent nature of flow in practical combustion devices. Turbulence is so complex that a detailed representation

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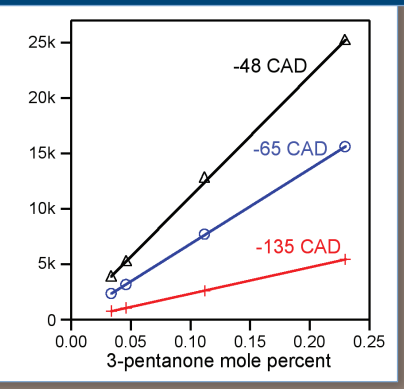

Figure 1. *Variation of spatially averaged LIF signal with tracer mole fraction and crank-angle position. Top dead center of compression is represented by 0 crank angle degrees (CAD).*

Sandia-Stanford collaboration demonstrates two-line PLIF engine diagnostic

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and Jordan Snyder have been working with Dick Steeper in the Automotive HCCI Laboratory to test an important new diagnostic for measuring temperature and exhaust gas residual (EGR) mole fraction in homogeneous-charge compression-ignition (HCCI) engines.

The planar laser-induced fluorescence (PLIF) diagnostic employs two wavelengths to simultaneously measure composition and temperature. Obtaining detailed temperature data in addition to more commonly measured fuel distribution data is essential for understanding, predicting, and controling the complex HCCI ignition process. The pair of wavelengths used in the diagnostic—308 nm produced by a XeCl excimer laser, and 277 nm obtained by Raman shifting the 248-nm output of a KrF laser—were carefully selected to optimize the diagnostic's sensitivity at conditions found in HCCI engines.

In the past few months, lasers and optics from Stanford have been installed in Steeper's engine laboratory, and tests of the diagnostic already have achieved significant and encouraging results. Following setup of the equipment, Sandia researchers investigated several factors influencing the system's performance. A frequently encountered problem with cylinder head reflectivity was dramatically reduced by coating pent-roof surfaces with carbon black. Flat-field uniformity was addressed by establishing a repeatable laser warm-up protocol. Linearity of the diagnostic was tested by varying tracer seeding levels, ambient densities, and bath-gas composition. Figure 1 demonstrates results of the linearity tests obtained in the motored engine. In the plot, an excellent straight-line trend of signal with EGR mole fraction is shown for measurements recorded at three different crank-angle positions (i.e., at three different gas densities).

Engine experiments were first conducted with spatially homogeneous composition and temperatures in the cylinder during motored operation. Using low tracer seeding levels (~0.1 mole% of the inlet charge), modest laser energies (~50 mJ), and an appropriate spatial resolution (~1 mm), strong signal-to-noise ratios were achieved throughout the compression stroke. The uniform temperature data allowed researchers to estimate a sensitivity better than 10 K (one-standard-deviation).

Increasing inlet charge temperature while cooling the head and cylinder allowed us to test the diagnostic under conditions of mild temperature stratification but uniform composition. Figure 2 presents an example of a single-cycle temperature measurement recorded 24 CAD (crank-angle degrees) after top dead center. In this image, good spatial detail is captured of a temperature field that varied about 40 K above and below the mean temperature of 709 K.

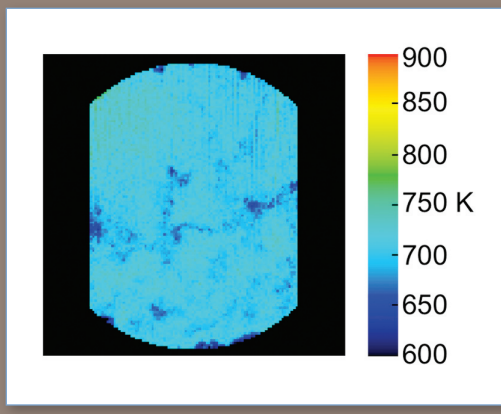


Figure 2. *Sample single-cycle temperature image recorded 24 CAD after top center of compression during motored operation. Tintake 410 K, Tcoolant 300 K, 1200 rpm.*

Temperature images as in Figure 1 are obtained by ratioing fluorescence signals from the two excitation wavelengths. Following temperature determination, simultaneous composition can be quantified using either or both of the fluorescence signals. To best test this capability we switched to conditions of uniform temperature and stratified composition by injecting an unseeded air stream into the uniformly seeded intake air. Figure 3 presents a time sequence of image pairs for these conditions recorded at three crank-angle positions starting during the intake stroke and continuing through compression. The composition images (left column) show that the initial intense stratification mixes out to some extent, but still retains substantial non-uniformities near the end of compression. The temperature images (right column) show the steady rise of the spatially uniform temperature during this period.

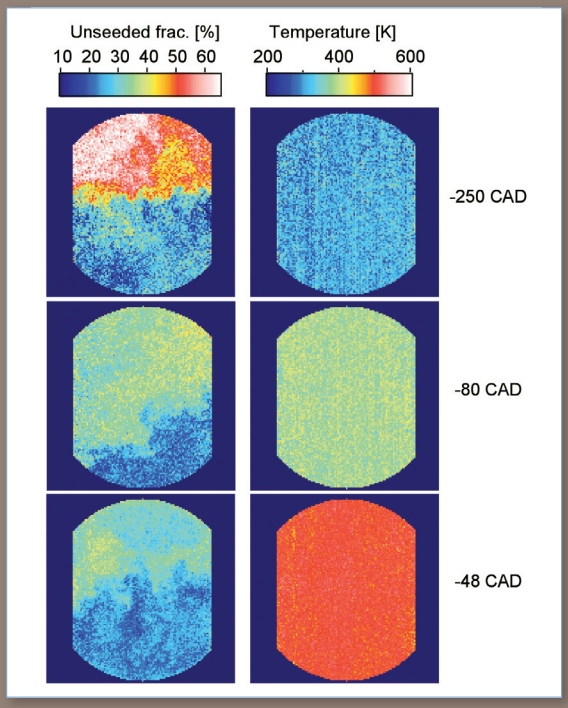


Figure 3. *Stratified (seeded and unseeded charge) intake composition during motored operation. Three simultaneous pairs of composition and temperature images were recorded at -250 CAD (top row), -80 CAD (middle row), and -48 CAD (bottom row). Average charge composition: 73% seeded, 27% unseeded.*

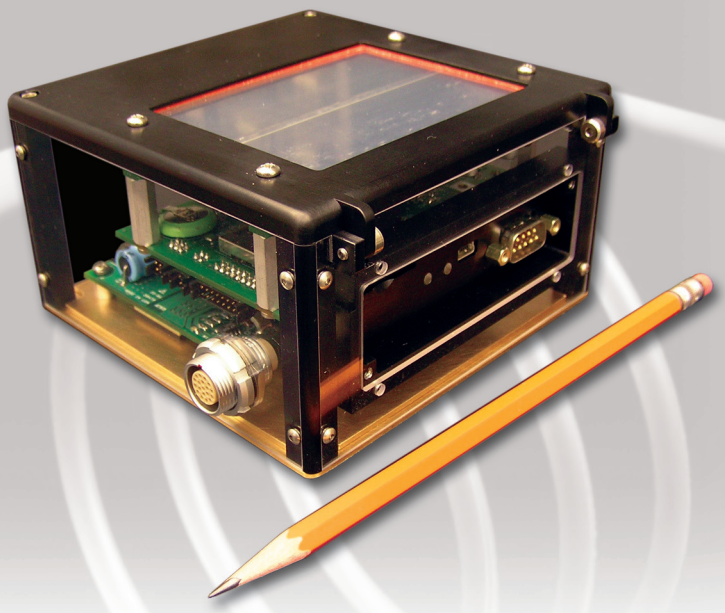
Experiments conducted with simultaneous temperature and composition non-uniformities were equally successful as those described above. Analysis of all the data collected is not yet complete, but initial indication is that the diagnostic is capable of providing valuable details of in-cylinder mixing of fuel, air, and EGR during HCCI operation. An important question to be addressed next is how well the diagnostic performs during fired operation.

Dahv Kliner and Jeff Koplow receive R&D 100 Award

CRF researchers Jeff Koplow and Dahv Kliner won the 2007 R&D 100 award for their Mode-Filtered Fiber Amplifier. Given by R&D Magazine, the R&D 100 Awards are known as "The Oscars of Invention."

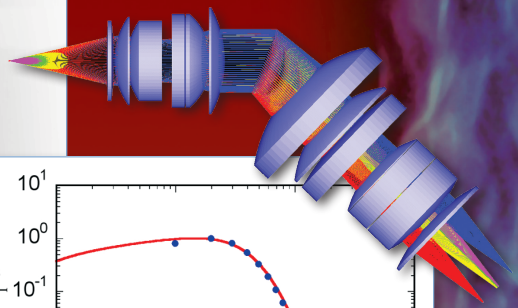
Conventional fiber lasers offer the advantages of high efficiency, compact size, ruggedness, and high beam quality, but they are restricted to low output powers. The Mode-Filtered Fiber Amplifier uses coiled fibers to dramatically increase output power while retaining all of the key benefits of fiber lasers. In 2000, Sandia and Naval Research Laboratory (NRL) researchers demonstrated that mode-selective bend loss from a coiled, large-core (multi-mode) fiber can act as a kind of distributed filter, suppressing all but the desired fundamental mode. Breaking the single-mode limit allowed fiber lasers to be scaled in power by more than a factor of 100.

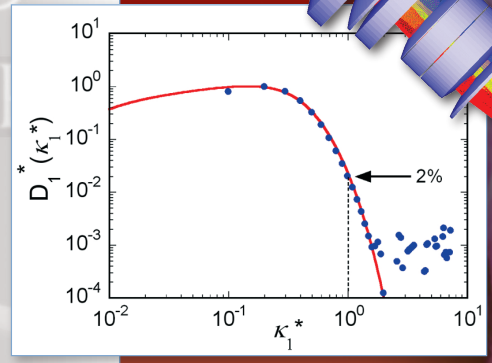
This discovery earned a patent in 2002 for Jeff Koplow, Dahv Kliner, and Lew Goldberg, the inventors listed on the current R&D 100 Award. The technique has become the de facto worldwide standard for power scaling of fiber lasers. The first commercial license for the invention was granted in 2005, and the first commercial products were offered by co-applicants Nufern and Liekki in 2006. Three other companies have licensed and commercialized mode-filtered fiber lasers. Mode-filtered fiber lasers have high electrical efficiency and optical gain, low waste-heat generation, broad wavelength coverage, and diffraction-limited beam quality (the theoretical limit) that is insensitive to vibrations, thermal fluctuations, and optical power level, all in a substantially smaller package than traditional solid-state laser sources. These advantages have allowed high-power fiber lasers to displace conventional lasers in numerous applications and have enabled a variety of new applications.



Guanghua Wang

Guanghua Wang completed a postdoc working with Rob Barlow in the Turbulent Combustion Lab. He started at the CRF in March 2005 and took a job with General Electric Global Research Center in Niskayuna, NY in June 2007. Wang played a major role in Sandia's recent research on measurements of scalar dissipation length scales in turbulent flames (CRF News article July/Aug 2006) and in the development of a new detection system from multiscalar line imaging (to be reported soon in the CRF News).

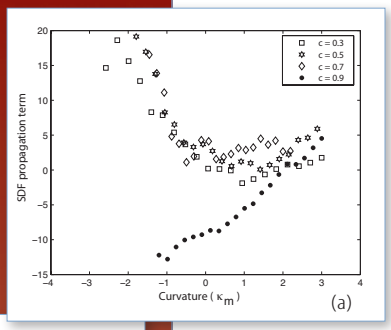


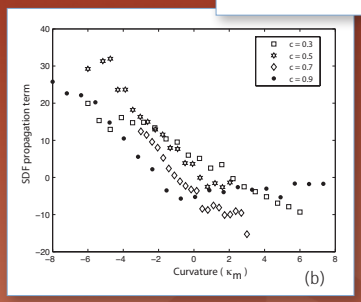


Images shown include a photograph of luminosity for the DLR-A turbulent $CH_4/H_2/N_2$ jet flame (right), an illustration of the optical design for the transmission spectrograph used for Raman scattering within the new detection system in the Turbulent Combustion Laboratory (center), and a graph showing close agreement between the measured thermal dissipation spectrum in the DLR-A flame and the model dissipation spectrum of Pope (see CRF News article July/August 2006).

Dr. Stewart Cant

Drs. Robert Stewart Cant and Nilanjin Chakraborty from Cambridge University have been collaborating with Jackie Chen and Evatt Hawkes to investigate the effects of tangential strain rate and curvature on the Surface Density Function (SDF) model of turbulent premixed flame combustion. They have compared the source terms within the SDF transport equation for lean methane-air and hydrogen-air flames using Direct Numerical Simulations (DNS) with detailed chemistry. They show that the behavior of the SDF propagation term displays significant differences between the two fuels . For methane flames, the propagation term is negatively correlated with curvature towards the reactant side of the flame and positively correlated with curvature towards the product side (Figure a). For hydrogen flames, the propagation term is negatively correlated with curvature throughout the flame brush (Figure b). These effects need to be accounted for in order to extend flame surface density modelling into the thin reaction zones regime where flames are subjected to intense turbulence.





Mean values of the SDF propagation term ($-\nabla.(S_d \vec{N} a)$) conditioned on curvature values on the c = 0.3, 0.5, 0.7, and 0.9 isosurfaces: (a) methane flame, (b) hydrogen flame.

Maurice Rojas visits CRF

Mathematician Maurice Rojas spent 3 weeks at the CRF working with David C. Thompson and Philippe Pébay on the problem of "fast and robust multivariate polynomial system solving," which has many practical applications, in particular to what Pébay and Thompson are trying to achieve in the field of scientific visualization for so-called higher order finite elements.

Left to right: David Thompson, Maurice Rojas, and Philippe Pébay

While at Sandia, Professor Rojas presented a 12-lecture seminar on the new theoretical developments and also participated in numerous technical discussions. The three researchers laid out a three-pronged approach that they hope will yield both novel theoretical results and practical developments. Pébay has already implemented one of these techniques, a method to solve univariate polynomial equations based on signed Sturm sequences and released this technique as a part of the Visualization Tool Kit (VTK), an open-source software package, for which Sandia is one of the main contributors: ***http://www.vtk.org/***. This technique has already been validated by demonstrating that it can solve problems that caused the traditional solver present in VTK to fail.

The researchers intend to continue their collaboration remotely until Rojas returns for another visit this winter.

Combustion study may impact chemistry of vision

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Figure 1 shows potential energy diagrams for the lightest (C_2H_3F) and heaviest (C_2H_3I) vinyl halides. The key difference between the two is the nature of the highest occupied molecular orbital (HOMO), from which an electron is promoted by the UV photon to the excited state. The HOMO, shown at the bottom of each diagram, is in both cases a molecular orbital that lies out of the molecular plane. For the three lightest vinyl halides, the HOMO is a π_{CC} bonding orbital (shown for vinyl fluoride), whereas for vinyl iodide the HOMO is a non-bonding I($5p_\perp$) orbital on the iodine atom.

All vinyl halides have a C=C double bond in the ground electronic state (A in Fig. 1), making it energetically costly to twist the molecule about this bond. However, when a photon (hν) excites one electron in C_2H_3F to the ($\pi^*_{CC}\pi_{CC}$) excited state (B), which is antibonding between the two carbon atoms, only a single bond remains between the two carbon atoms. This excited state electronic configuration induces a twisting motion between the CH_2 and CHF planes of the molecule, driving the system toward (C), with a φ = 90° dihedral angle. At this configuration there is a conical intersection (D) between the ground and excited state surfaces, which funnels population efficiently back to the ground electronic state (E). Once on the ground electronic state, C_2H_3F dissociates over a transition state barrier (F) to form HCCH + HF (G). A similar mechanism occurs in C_2H_3Cl and C_2H_3Br, but in these molecules, there is also some branching to the atomic channel via the excited state pathway (H).

By contrast, in vinyl iodide, the HOMO is a non-bonding I($5p_\perp$) orbital on the iodine atom, as shown in the right panel of Figure 2 at (J). UV excitation of one electron from this orbital forms an ($\pi^*_{CC}n_\perp$) excited state. Although placing one electron in an antibonding π^* orbital weakens the CC bond, the removal of an electron from the non-bonding I($5p_\perp$) orbital on the iodine atom has essentially no effect on the CC bond strength. As a result, the excited state of vinyl iodide effectively has 1.5 bonds between the two carbon atoms (K). This difference, in comparison to C_2H_3F, means that vinyl iodide has a planar equilibrium geometry in the excited state.

Because it now costs energy to twist the molecule about the CC bond, the twisted configuration at (L) is much higher in energy than the same configuration on the ground electronic state, and therefore C_2H_3I has no efficient path to return to the ground electronic state. Instead, dissociation on the excited (σ^*n) state, which is repulsive along the C – I bond, efficiently breaks the C – I bond on a timescale faster than the rotation of the parent molecule (~ 1 ps), leading to the atomic products observed at point (M).

These results may affect our understanding of chemical systems in which photoisomerization around a C=C double bond is possible. The example of vinyl iodide shows that the particular substituent adjacent to the double bond can drastically change the nature of the molecular orbitals, and therefore open or close photochemical pathways.

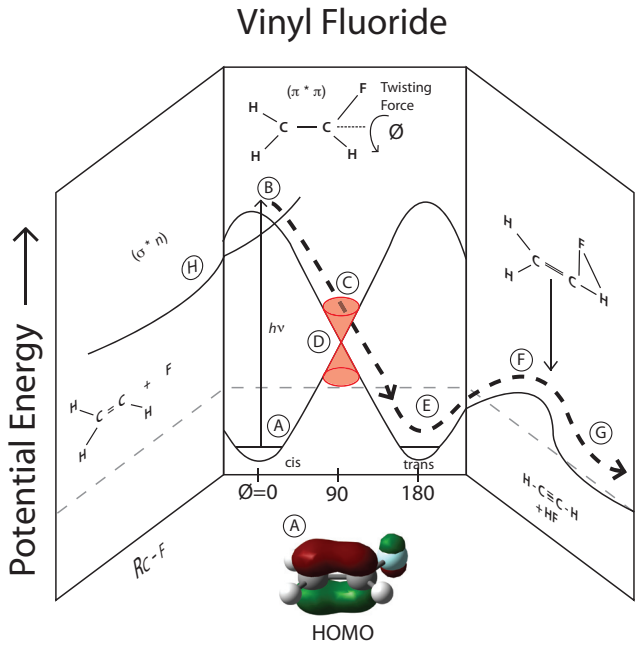

Figure 1. *Molecular orbital and potential energy diagram for the photodissociation of C_2H_3F. Twisting about the C - C bond in the excited state leads to HF + HCCH products.*

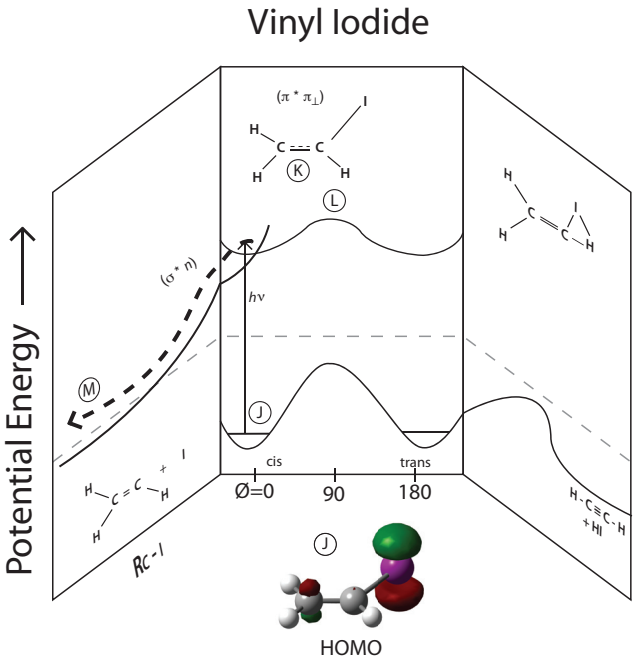

Figure 2. *Molecular orbital and potential energy diagram for the photodissociation of C_2H_3I. The partial π - bond in the excited state inhibits twisting about the C - C bond, resulting in only C_2H_3 + I product.*

Conjectured turbulent-burning-velocity law proven mathematically

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short of detailed simulation seems unattainable, but tractable simplification is achieved by viewing it as a random process described by a small number of statistical properties. For maximum simplicity, Mayo assumed a statistically homogeneous, isotropic flow. In this case, the minimal statistical parameterization is a single number, the root-mean-square velocity fluctuation u′.

It is an empirical fact, with some theoretical support, that expressing the bulk burning velocity uT as a function of u′ is a useful approximation. However, the dependencies of the functional form on flow and flame structure are not yet well understood. As a step toward understanding these dependencies, we idealized the flame as a front propagating at a constant local speed S, with no back-coupling to the flow (e.g., thermal expansion). This assumption eliminated flame-structure effects. On this basis, Mayo sought the regime corresponding to minimal dependence of uT on flow properties. Mayo determined this regime to be the weak-turbulence regime u′<< S. This regime is not of direct practical interest, but the analysis of this regime identified another flow property, in addition to u′, that is influential in all flow regimes, including those of practical interest. The additional property is the spatial autocorrelation function of flow velocity, denoted A(x), which is a function of a spatial variable x.

This recearch thus established that the minimal flow parameterization required for a complete model (or theory) of uT consists of the function A(x) as well as quantity u′. This analysis has certain additional significant implications.

The genesis of this work was based the conjecture made in 1992 by Kerstein (supported by computations by Sandia retiree Bill Ashurst) that (uT/S)-1 is proportional to the 4/3 power of u′/S in the weak-turbulence regime. Subsequently, a counterexample was identified, leaving the question still not wholly answered. The counterexample involves a form of anisotropy that is unphysical and therefore not of interest.

From this starting point, Mayo showed that the 4/3 power dependence is an exact result for isotropic flows subject to mild regularity conditions, and for most anisotropic flows. He accomplished this by considering the trajectory of a point on the flame front (in optics terminology, a ray). In the weak-turbulence regime, individual fluid motions induce such slight perturbations of a ray that a large number of perturbations are needed to significantly deflect the ray. Invoking the law of large numbers, this suggests that the effect of the flow corresponds to a white-in-time (history-independent) forcing relative to ray-deflection time scales. However, mathematical consistency requirements (e.g., no spurious divergences) constrain the conditions under which this outcome is valid, such that the 4/3 power dependence is found to be the only allowed dependence. The optics analogy is substantive as well as suggestive.

The analysis demonstrates an equivalence of the weakly turbulent combustion problem to geometrical optics in a motionless medium with small variations of the index of refraction. In the latter case, weak variability of the medium is a regime of practical interest. Other direct applications are sub-surface and oceanic acoustic propagation.

Another outcome was the determination that front advancement is governed by the white-noise-driven Burgers equation, an idealized hydrodynamic equation that omits pressure effects. This finding enabled adaptation of quantum-field-theory methods previously applied to the Burgers equation to estimate the coefficient of proportionality in the 4/3 power dependence. This adaptation led to the identification of the key role of A(x). Numerical simulations verified that the field-theory estimate is usefully accurate.

Because uT is an increasing function of S, the field-theory result implies a useful constraint on the value of uT in the strong-turbulence regime. A more fundamental aspect of the field-theoretic result is its functional form, which suggests a strategy for improving the "renormalization" method that is currently the most promising theoretical tool for analysis of that regime.

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