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MOLECULAR BEAM STUDIES OF VOLATILE LIQUIDS AND FUEL SURROGATES USING LIQUID MICR

**Gilbert Nathanson
UNIVERSITY OF WISCONSIN SYSTEM MADISON WI**

**12/23/2014
Final Report**

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14. ABSTRACT Our motivation is to explore the heating, evaporation, and aging of volatile fuel droplets, which evaporate and combust at pressures and temperatures up to 30 atm and 2000 K in a jet engine. A microscopic, "blow by blow" description of these events can be obtained by monitoring the evaporation of liquid fuel inside a vacuum chamber and by bombarding it with ambient gases to measure collisional heating. We successfully carried out two separate sets of experiments over the grant period: 1) studies of collisional heating of fuel droplets by ambient gases and 2) studies of super-Maxwellian helium evaporation from hydrocarbon liquids and jet fuels to investigate the packing and attractions of molecules at the surfaces of fuel droplets. During the course of these experiments, we developed the liquid microjet technique for investigating volatile liquids in vacuum-based scattering experiments.					
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Molecular Beam Studies of Volatile Liquids and Fuel Surrogates Using Liquid Microjets

Gilbert Nathanson, Department of Chemistry University of Wisconsin
AFOSR Grant FA9550-10-1-0176 from 05/15/2010 to 08/31/2014

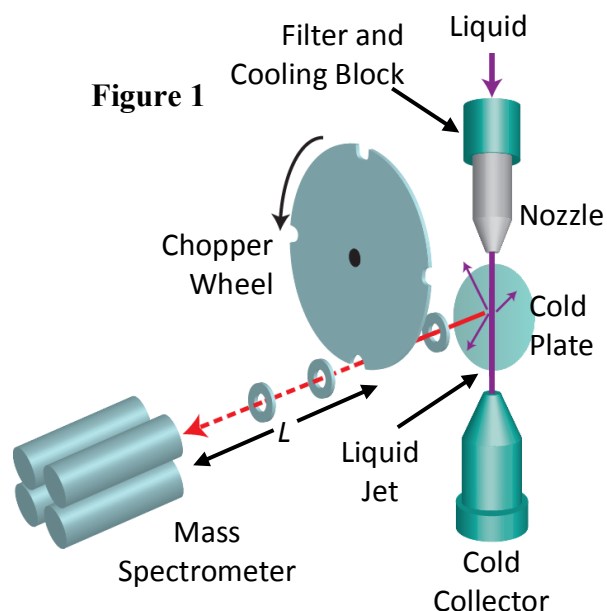
I am delighted to report that we have carried out the experiments proposed during the grant period and made two fundamental discoveries about the behavior of jet fuel droplets: 1) collisional heating of fuel droplets by ambient gases is extremely efficient and 2) the additives in the military jet fuel JP-8 do not segregate to the surface of the fuel in ways that would alter the dynamics of evaporation from the commercial jet fuel Jet A. These results are outlined below.

Exploring Fuels in Vacuum using Liquid

Microjets

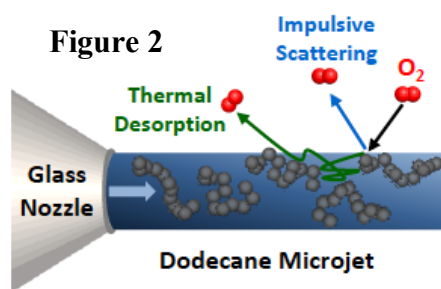
The chief technical advance over this grant period is the development of narrow diameter microjets for the investigation of volatile hydrocarbon liquids inside a vacuum chamber. These jets, narrower than a human hair, are typically 10 – 40 μm in diameter. Their small surface area and high curvature allow evaporating molecules to escape from the liquid without colliding with each

other in the vapor cloud surrounding the jet. The apparatus is pictured in Figure 1. Dissolved gases evaporate from the jet during its exposure to the vacuum, and a fraction are sliced into pulses by a chopper wheel whose time of arrival are monitored by a mass spectrometer. The upper limit to the liquid vapor pressure is about 1 Torr; beyond this, the solvent molecules will begin to collide with each other in the vapor above the jet. We have used this microjet method to investigate a wide range of high-vapor pressure liquids, including octane, isooctane, dodecane, squalane, methylnaphthalene, ethylene glycol, and Jet A and JP-8 fuels themselves. Detailed discussions of the microjet technique are carried out in the following publications.

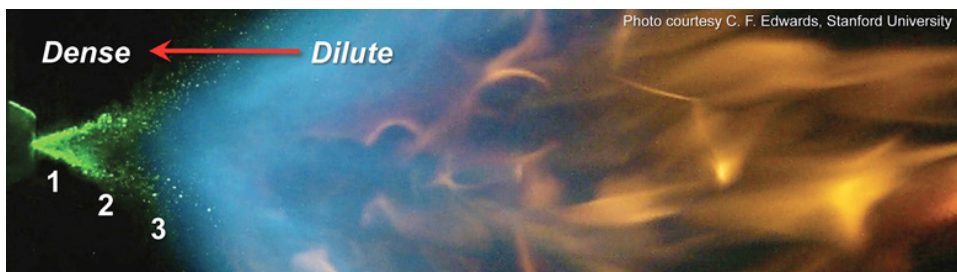


1) “**Inert Gas Scattering from Liquid Hydrocarbon Microjets**”, Diane K. Lancaster, Alexis M. Johnson, Daniel K. Burden, Justin P. Wiens, and Gilbert M. Nathanson, *Journal of Physical Chemistry Letters*, **4**, 3045 (2013).

This is the first molecular beam study of controlled collisions between gas molecules and a highly volatile liquid (dodecane). This publication demonstrated the feasibility of using liquid microjets for gas-liquid scattering experiments. The signal to noise is indeed very low because of the small diameter of the microjets, but we are presently improving the apparatus to reduce the signal averaging time. In the experiments reported here, we directed Ne atoms and O₂ molecules at liquid microjets of pure dodecane (C₁₂H₂₆) and pure squalane (C₃₀H₆₂), in vacuum and monitored the recoiling Ne or O₂ by a mass spectrometer (as shown schematically in Figure 2).



The microjet experiments allow us to address a fundamental question: how do fuel droplets heat up and evaporate in a jet engine? This heating process is shown in the picture below;



heating and evaporation occur within 1 ms of fuel leaving the fuel injector. This atomization process is often the limiting process in combustion, which occurs only in the gas phase.

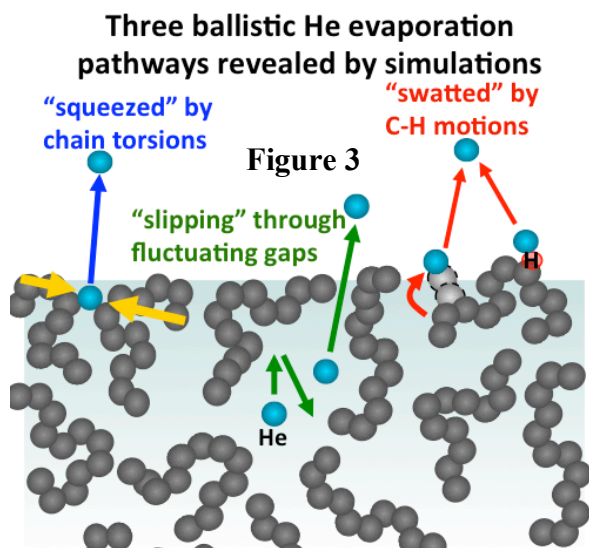
Our key result is that energy transfer is extremely efficient: greater than 75% of the translational energy of the O₂ molecules is transferred to liquid dodecane and squalane, with little difference between the short and long-chain liquids. These results imply that the surfaces of the liquids do not impose a barrier to gas-surface energy transfer and therefore that gas-liquid heating occurs quickly inside the jet engine. The rate limiting step in this heating process is likely to be heat flow through the gas phase itself, as the high thermal conductivity of the liquid

fuel will rapidly distribute thermal energy throughout the fuel droplets.

These experiments also suggest a possible aging mechanism that we were unable to find in the combustion literature. It may be possible that simple radicals created by combustion in the gas phase, such as H, OH, and CH₃, sometimes return to the droplet through random scattering and react with surface hydrocarbon molecules, breaking them into smaller species. Thus, the fuel molecules that evaporate may not always be the original fuel molecules but rather more reactive cracks. We hope to discuss this possibility with engineers that model fuel combustion.

2) **“Ballistic Evaporation and Solvation of Helium Atoms at the Surfaces of Protic and Hydrocarbon Liquids”**, Alexis M. Johnson, Diane K. Lancaster, Jennifer A. Faust, Christine Hahn, Anna Reznickova, and Gilbert M. Nathanson. *Journal of Physical Chemistry Letters*, **5**, 3914-3918 2014.

During the course of our experiments, we stumbled on a remarkable discovery: helium atoms dissolved in liquids evaporate at super-Maxwellian speeds, whose average energies exceed the expected value of $2RT$. We discovered this result when using helium gas to pressurize the liquids in forming the fast-moving microjets and monitoring the evaporation of the He atoms. This was an astonishing result because, prior to these experiments, all gases had been observed to evaporate in perfect Maxwellian distributions. Presently, three theory groups are struggling to interpret the microscopic mechanisms: Ilan Benjamin (UC Santa Cruz), Jim Skinner (UW-Madison), and Sven Koehler (Manchester University, England). Their studies have not yet converged, but three ideas stand out, as shown in Figure 3: the He atoms may “squeeze” or “slip” through fluctuating gaps or be “swatted” by motions of the C and H atoms of the hydrocarbon molecules. A remarkable



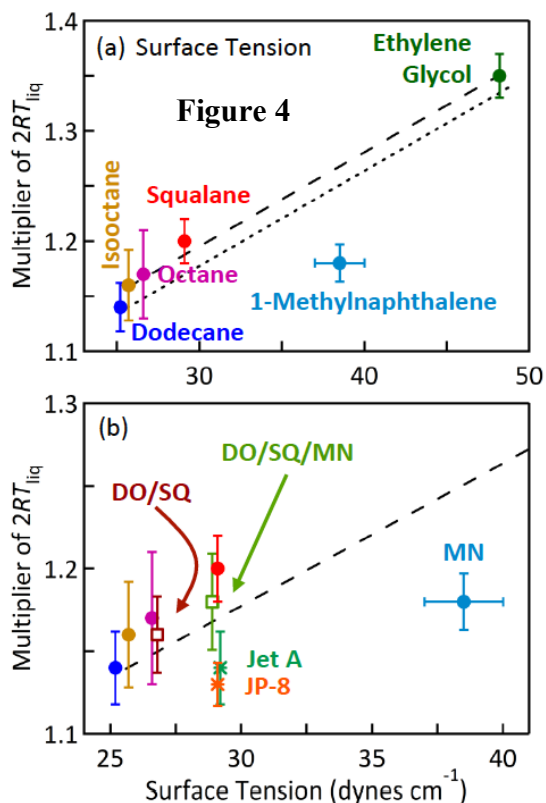
implication of these studies is imposed by detailed balance: each trajectory may be reversed, implying that our evaporation studies also indicate how helium atoms “ballistically” dissolve into liquids.

Our most important finding is the wide variation in helium evaporation energies from different liquids, ranging from $1.14 \times 2RT$ for dodecane to $1.7 \times RT$ for an 8 M LiBr solution in water (versus just $2RT$ for gases such as Ar, O₂, N₂, and CO₂). The extra evaporation energy appears to correlate with liquid surface tension, perhaps because this quantity controls the size and lifetime of fluctuating gaps at the surface from which He atoms escape. This correlation is investigated in detailed in the manuscript described below.

3) “**Probing Gas-Liquid Interfacial Dynamics by Helium Evaporation from Hydrocarbon Liquids and Jet Fuels**”, Diane K. Lancaster, Alexis M. Johnson, Keaten Kappes, and Gilbert M. Nathanson. Submitted to the *Journal of Physical Chemistry C*, December 12, 2014.

This manuscript describes in detail the microjet technique and its application to helium evaporation from octane, isooctane, dodecane, squalane, 1-methylnaphthalene, Jet A, and JP-8. We first review the basic operation of liquid microjets in vacuum, followed by detailed calculations of evaporative cooling as the liquids vaporize, breakup of the jet into droplets as they minimize their surface area, and the number of collisions that occur within the vapor cloud surrounding the liquid jet. This analysis leads to criteria for selecting the temperature and nozzle radius for producing stable jets in vacuum.

Figure 4 depicts the measured correlation between the average helium evaporation energy and



the surface tensions of the liquids. This evaporation energy is expressed as a multiplier or quotient $\langle E_{\text{evap}} \rangle / 2RT_{\text{liq}}$. Panel a shows how the average He energy increases steadily with liquid surface tension. The aromatic liquid, 1-methylnaphthalene (MN), a key component of JP-8, appears to be exceptional and falls below the curve. This is shown by the dotted fit (including MN) and the dashed fit (excluding MN). We conjecture that MN is unique because it is made of two fused phenyl rings that stack perpendicularly at the surface; the He atoms may be able to slip between these rings more easily than they move through compact and meandering alkyl chains.

Panel b shows the He evaporation energies from mixtures of dodecane (DO) and squalane (SQ), as well as from Jet A and JP-8. Our most important result is that He atoms evaporate from Jet A and JP-8 with the same average energy within the error bars. This result implies that the additives in JP-8 (such as fuel system deicer, chemically similar to ethylene glycol) do not alter the dynamics of He atom evaporation. We also measured nearly identical surface tensions for the two fuels. The similar surface tensions and He evaporation energies for Jet A and JP-8 together imply that the surface compositions and interactions among hydrocarbon molecules must be similar for the two fuels. These observations in turn suggest that fresh JP-8 fuel spray will evaporate like Jet A fuel spray, at least until the droplets shrink and the additives are forced into the surface region or separate into a new phase.

Student Participating in Research during the Grant Period

This research was primarily carried out by graduate students Daniel Burden, Justin Wiens, Alexis Johnson, and Diane Lancaster under my direction. Daniel currently teaches at Thomas Jefferson High School in Alexandria, VA, Justin is presently a postdoc with Al Viggiano, Alexis is presently a postdoc with Peter Stair at Northwestern University, and Diane just began as a postdoc with Steve George at the University of Colorado. The AFOSR grant also funded Anna Reznickova, who was a graduate student with me for one year before switching fields to Environmental Policy. Support was also provided for a short time for Michael Shaloski and WenTsung Huang, who assisted with the experiments. Undergraduate students Ross Edel, Matt

Melvin, and Keaten Kappes measured surface tensions for the experiments.

Future Experiments

1) We are eager to measure the angular distribution of He atoms that evaporate from each liquid; these measurements will provide key structural information about the orientation and packing of hydrocarbon molecules at the surface, as well as providing a stringent test of the simulations. We are presently setting up for these measurements using liquid squalane and a planar rather than circular jet.

2) Perhaps the greatest remaining challenge in fuel evaporation concerns the behavior of droplets at high temperatures and pressures near the critical point, where the liquid-gas interface becomes broadened and volatile fuel components internally boil and explode. This behavior is shown in Figure 5 for hexane boiling out of a hexane/hexadecane droplet. Recent research indicates that this regime is common for internal combustion, diesel, and jet fuel engines (Dahms and Oefelein,

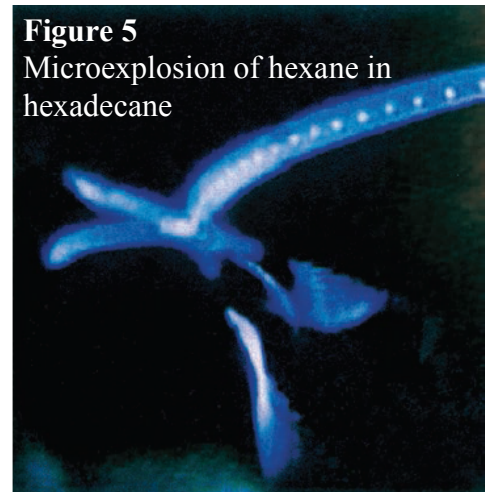


Figure 5
Microexplosion of hexane in
hexadecane

Physics of Fluids **25**, 092103 (2013)) and that microexplosions can occur in hot droplets (Mikami and Kojima, Proceedings of the Combustion Institute **29**, 551 2002). We plan to investigate these explosive disintegration of the droplet by monitoring evaporation of hexane from hexane/squalane mixtures above the critical point of hexane (507 K and 30 atm). These measurements may provide substantial evidence for a kind of “molecular geyser” as hexane boils within the droplet and rips holes in it, as shown in Figure 5. We hope that a deeper understanding of this explosive boiling may lead to better ways of atomizing fuel within the combustion zone and leading to more efficient fuel burning.

1.

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Gilbert M. Nathanson

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08/31/2014

Abstract

Our motivation is to explore the heating, evaporation, and aging of volatile fuel droplets, which evaporate and combust at pressures and temperatures up to 30 atm and 2000 K in a jet engine. A microscopic, "blow by blow" description of these events can be obtained by monitoring the evaporation of liquid fuel inside a vacuum chamber and by bombarding it with ambient gases to measure collisional heating. We have carried out two separate sets of experiments over the grant period:

1) Collisional heating has been investigated by bombarding liquid dodecane, a single component fuel surrogate, with O₂ molecules and measuring the residual energy of the recoiling O₂. We find that the gas-fuel energy transfer is extremely efficient, implying that fuel droplets heat up as fast as energy can be transferred to them from the gas phase. No difference was observed between liquid dodecane (C₁₂H₂₆) and liquid squalane (C₃₀H₆₂), further implying that fuels composed of short and long-chain molecules similarly absorb energy from the surrounding gas.

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2) We made the startling discovery that dissolved helium atoms evaporate “ballistically” from liquids, reflecting the packing and attractions among the surface molecules. The similar helium evaporation speeds from the jet fuels Jet A and JP-8 imply that the additives in JP-8 do not alter the surface composition and dynamics of evaporation of the hydrocarbon fuel components. These observations suggest that fresh JP-8 fuel spray will evaporate like Jet A fuel spray, at least until the droplets shrink and the additives are forced into the surface region.

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