Spectrometric System for Characterizing Drop and Powder Trajectories and Chemistry in Reactive Flows

JERRY C. CABALO,* JOHN SCHMIDT, JOST O. L. WENDT, and ALEXANDER SCHEELINE†

Department of Chemistry, University of Illinois at Urbana-Champaign, 600 S. Mathews Ave., Urbana, Illinois 61801 (J.C.C., A.S.); and Department of Chemical and Environmental Engineering, University of Arizona, 1133 N. Campus Dr., Tucson, Arizona 85721 (J.C.C., J.S., J.O.L.W.)

An instrument for emission, fluorescence, and scattering diagnostics of a 22 kW gas/air thermal reactor is described. Z-pair parabolic mirrors provide diffraction-limited imaging in field center, with worst-case blur over a 12.8 mm field of view having a radius of 0.044 mm rms. Either full-field filtered or transverse line dispersed viewing can occur simultaneously. Dispersion is achieved using a 2-m spectrograph *f*-matched to the feed optics. Examples of data show non-axisymmetric flow in a nominally laminar flow system, drop shapes *in situ*, and Mie scattering from soot.

Index Headings: Flame diagnostics; Planar laser-induced fluorescence; Spectroscopy in harsh environments; Imaging; Drop vaporization.

INTRODUCTION

Metal-bearing solutions and slurries can pose environmental hazards. Among the most acute of these hazards is the accumulation of radioactive wastes, held in underground steel tanks at locations such as Hanford, Washington, and the Savannah River Site at Aiken, South Carolina.¹⁻³ Vitrification of radioactive wastes, either as glass logs⁴ or cement,⁵ is the approach most actively being followed to sequester radionuclides over the millennia required for decay to negligible activity levels. An important step in preparation of vitrified material is removal of water and organic material, resulting in volume reduction. Among the ways to perform solvent removal, that simultaneously destroys organic matter, is thermal treatment. This process simply consists of spraying the waste into a high temperature ($T > 1800$ K) reactor and adding powdered sorbent material. Water is vaporized, organics are oxidized to water and carbon dioxide, and metallic species are oxidized. Scavenging of metal ions by kaolinite⁶⁻⁹ prior to cooling and oxide formation is a promising technology for high-efficiency collection of gas-phase radionuclides. Under optimized conditions, destruction/recovery efficiencies (DREs) of up to 99.99% of metal ions in an entering waste stream can be scavenged.

Considering the hundreds of millions of curies in the millions of gallons of waste,³ a DRE of 99.99% scavenging is entirely unacceptable. Understanding the cause of the 0.01% unscavenged fraction and devising means for its reduction are essential if thermal processing is to be used for nuclear waste treatment. Our hypothesis is that a small fraction of large (>200 μm in diameter), that

is, "rogue", drops originating from the input liquid stream or formed by coalescence in the reactor are responsible for the 0.01% unscavenged metals. These drops avoid hot zones in the reactor, resulting in either incomplete vaporization or vaporization in a zone with insufficient temperature to vaporize the metal contents. The metals form small particulates that easily circumvent particle traps such as filters and cyclones.¹⁰ Drop dynamics in analytical flames and plasmas has been studied for many years, including work by Hieftje (e.g., Refs. 11-13), Farnsworth,¹⁴ and Olesik (e.g., Refs. 15-18). To test the rogue drop hypothesis requires the ability to generate drops, both as sprays and as monodisperse streams, to measure drop size as a function of position, to measure drop and gas-phase temperature, and to observe speciation in the reactor, including free atoms, small molecules, and soot. With the exception that a lack of a tunable laser prevented observation of free atoms, the apparatus reported here is capable of all these measurements. Drop generation is by use of an electronically driven oscillating piezoelectric bimorph.^{10,11} Temperature measurement within drops is based on exciplex fluorescence.¹⁹⁻²⁵ While we had hoped to measure soot temperature via laser-induced incandescence (LII),²⁶⁻²⁸ the dispersion of the available spectrograph is more appropriate for atomic or molecular line/band emission rather than the LII continuum.

We now describe the flame diagnostics instrument and give examples of its use.

DESIGN PRINCIPLES

To have freedom from chromatic aberration and because of the success of all-reflective spatial and temporal resolution spectrometric systems in recent years, only reflective focusing elements were employed. The only transmissive components are windows in the sides of the reactor and one beam splitter.

The excitation laser beam was focused to a sheet illuminating a plane passing through the axis of the cylindrical reactor (Fig. 1). A cylindrical mirror, dielectric-coated for maximum reflectivity at 308 nm, converted the rectangular (24 mm by 6 mm) beam from the excimer excitation laser to a 50-mm-high, 1.6-mm-thick illumination sheet. The central plane of this sheet is the object plane for the observation optics.

Stigmatic imaging was based on the work of Goldstein and Walters²⁹ as later implemented by Klueppel et al.,³⁰ Hsu et al.,³¹ Scheeline et al.,³² and Scheeline et al.³³ In this arrangement, images are relayed from point to point

Received 4 March 2002; accepted 4 June 2002.

* Current affiliation: U.S. Army Research Laboratory, Aberdeen, MD.

† Author to whom correspondence should be sent.

TABLE I. Components used in fluorescence, scattering, and emission apparatus. All positions are referenced to the center of the observation point in the reactor when viewed through the top port, just below the combustor inlet. Axes are for a right-handed Cartesian system, with fluoresced or scattered light observed when directed along the x axis, laser entering along the +y axis.

Component	Description	Vendor	x (mm)	y (mm)	z (mm)
Excimer laser	308 nm XeCl	Lambda Physik	159	1465.00	-1016.54
Folding mirror 1	dielectric, 308 nm	Melles Griot, Irving, CA	0	1465.00	-1016.54
Folding mirror 2	dielectric, 308 nm	Melles Griot	0	943.57	-1016.54
Cylindrical mirror	50 in. f.l. dielectric	Fabrication: Harold Johnson Optical Labs, Gardena, CA; Coating: Acton Research	0	943.57	477.07
Folding mirror 3	3 in. diameter dielectric	Melles Griot	0	793.40	0
Reactor entrance window (outer surface)	2 in. diameter quartz, AR coated one side	CVI Laser Corp., Albuquerque, NM	0	730	0
Observation point			0	0	0
Reactor exit window (outer surface)	2 in. diameter quartz, AR coated one side	CVI Laser Corp.	723.22	0	0
Folding mirror 4	3 in. diameter Al mirror, MgF ₂ coating, 310 nm optimized	Melles Griot	793.65	0	0
Collimation parabola 1	50 in. (1270 mm) f.l. f/15 parabola	Astronomically Xenogenic Enterprises, (AXE) Tucson, AZ	837.33	0	474.39
Collimation parabola 2	50 in.	Same	837.33	0	-1422.41
Folding mirror 5	3 in. Al mirror	Melles Griot	903.61	0	-698.51
Beam splitter		CVI Laser Corp, Albuquerque, NM	1485.24	0	-698.51
Folding mirror 6	3 in. Al mirror	Melles Griot	1485.24	127	-698.51
Z-pair 1 mirror 1	600 mm f.l. f/15 parabola	3B Optical Co.	1034.24	127	-698.51
Z-pair 1 mirror 2	600 mm	Same	1866.08	254.7	-698.51
ICCD	IMAX-512 fiber-optic coupled 512 × 512, 18 μ m pixel	Roper Scientific	1266.07	254.7	-698.51
Z-pair 2 mirror 1	1000 mm f.l. f/15 parabola	3B Optical Co.	2455.72	0	-698.51
Z-pair 2 mirror 2	1000 mm	Same	1602.12	0	-622.33
Folding mirror 7	3 in. Al mirror	Melles Griot	2358.61	0	-622.33
Spectrograph entrance slit	2 m f.l. 1200 g/mm grating	Minuteman Labs, Acton, MA	2358.61	257.3	-622.33

served to enhance eye safety, as poly(methyl methacrylate) absorbs 308 nm laser light), and pumped dry HEPA-filtered air into the enclosure. Despite months of experiments on coal dust combustion taking place on both the reactor in which we observed drop dynamics and in an adjacent reactor, which together left a thick coating of dust on the outside of the spectrograph and Lucite box housings, the optical path remained free of detectable dust and the mirrors never suffered damage.

The only excitation yet employed on this apparatus is the 308 nm XeCl laser band (Lambda Physik COMPex 201, Ft. Lauderdale, FL). Ultraviolet wavelengths were chosen so that signals would be well away from the blackbody continuum emitted by the reactor walls. Pulsed illumination assisted in temporal selection against continuum while assisting in obtaining strong signals from single drops. Signal-to-noise ratio calculations suggested that illumination at over 10 mJ per pulse would be required to obtain adequate LIF, LII, and Mie scattering signals. Budget dictated that a tunable laser with this power was out of the question. The only laser meeting all these constraints is an excimer laser. The desire to

excite both OH (for flame temperature measurement) and some convenient metal atom (Al at 308.4 nm or Cu at 307.47 nm) led to our choice of XeCl. We plan to obtain a tunable dye laser in the future. The only components that must be changed to accommodate tunable operation are the mirrors that relay and focus the laser beam to the mid-plane of the reactor.

COMPONENTS, ASSEMBLY, AND CHARACTERIZATION

Optical components are summarized in Table I, with off-axis angles shown in Table II. A reviewer noted that the Minuteman 2 m spectrograph is uncommonly used in flame diagnostics, but that the Jarrell-Ash 0.25 m Ebert monochromator/spectrograph is widely employed. The setup using such an instrument is that shown in the tables except that the lower astigmatism of the short focal length Ebert mount means that the off-axis angle for the over/under mirror pair is 3.78° instead of 2.55°. This translates the upper 1000 mm f.l. mirror 280 mm closer to the lower mirror, pushing the last 45° folding mirror a similar distance away from the reactor. Because the Ebert's mirror is illuminated off-axis, the computed ultimate spatial resolution is poorer (geometric spot diameter in field center, 50 μ m) than in the system we built and characterized.

Most planar laser-induced fluorescence apparatus use cylindrical lenses to focus the incident laser beam. We chose to use a cylindrical mirror (Harold Johnson Optical Labs, Gardena, CA), as we needed a focal length of 50 in., a distance not commonly available, and also wavelength-dependent in a transmitting optic. The high effec-

TABLE II. Mirror off-axis angles.

Mirror	Off-axis angle
50 in. cylinder	3.00°
50 in. parabolas	3.00°
600 mm parabolas	4.364°
1000 mm parabolas	2.55°
2 m spectrograph collimator	2.71°
2 m spectrograph camera	3.25°

posite the admission port for the laser. The flame igniter also used the same port, so placement of the beam dump could only occur after the combustor was ignited.

Gated detection is essential for several reasons. First, while the optics bench is covered with black cloth, stray room light contributes some signal if long integrations are used. Second, while observations are typically in the mid-UV, where 1800 K blackbody continuum is negligible, only broadband filters have been used to date. Time gating enhances the signal-to-background ratio by synchronizing detector response to laser firing. Time gating could be used to differentiate fluorescence, laser-induced incandescence, and laser-induced plasma emission from scattering, but this has not been successfully observed to date. The intensifier was chosen for optimal ultraviolet response. The IMAX-512 has the image intensifier pixels on 25- μm centers; the output bonded fiber-optic array tapers to the 18- μm CCD pixels (Thomson, 5×10^5 e- full well capacity, 16-bit ADC). On/off gating ratio was not measured, but is claimed to be $> 10^4$. Thermo-electric cooling was adequate; dark current was not significant in any experiments reported here.

Many mechanical components were fabricated at the University of Illinois School of Chemical Sciences Machine Shop and shipped to the University of Arizona as a flame spectroscopy toolkit. The University of Arizona Department of Chemical and Environmental Engineering Machine Shop was employed to fabricate the Lucite housings, gas handling system, reinforcements to stabilize the cart holding the excimer laser, and an assortment of other components not anticipated in the original design. The combination of the large capacity at Illinois with the contiguous access to both skilled personnel and equipment at Arizona were necessary for the successful completion of the instrument. In a field not noted for research at remote facilities, managing instrument completion proved to be an exercise in management and co-operation on an unfamiliar scale.

Both commercial and in-house software was used for data acquisition and instrument control. Image data from the Princeton Instruments digital camera was recorded using *Winspec* software written by the manufacturer. Computer control of the spectrograph was achieved using a Computer Boards CIO-CTR05 digital I/O card with C++ software to pulse the stepper motor. Spectral data was recorded using either the Princeton Instruments CCD camera or a photomultiplier tube. Again, the commercial software package *Winspec* was used in conjunction with the ICCD camera. Data from the photomultiplier tube was digitized and integrated using a Tektronix TDS 220 digital oscilloscope controlled with C++ software.

Monodisperse streams of large drops were formed by a specially designed vibrating orifice drop generator. This system is a variation of the system used by Hanlon and Melton.³⁹ The generator body consisted of a brass ring with a diametrically opposed nozzle assembly and feed tube. The two open ends of the ring were sealed with piezo-electric buzzer units (Radio Shack, model 273-064) driven by a Hewlett Packard 214B square wave generator. The nozzle assemblies were formed from ruby orifices with diameters between 190 and 254 μm (Byrd Scientific), fixed at the end of a conical brass nozzle, which in

turn was brazed to the brass ring. The feed tube and the nozzle assembly formed the axis of the generator.

The generator could be operated in two modes: vibrating-orifice-drop-generator mode (VODG) and drop-on-demand mode (DOD). VODG mode was capable of forming drop arrays with drop diameters ranging from 350 to 750 μm by vibrating the assembly at frequencies ranging from 1 kHz to 20 kHz. Liquid was fed to the drop generator from a sealed vessel pressurized with compressed air up to 10 psig, though the typical operating pressure was 5 psig or less. The monodisperse drop stream was formed when the buzzer units were synchronously vibrated at the proper frequency. At frequencies less than 1 kHz, no monodispersity was observed, and at frequencies higher than 15 kHz monodispersity was lost as drops coagulated due to decreased drop spacing. In DOD mode, only a light backing pressure was used in the reservoir, and this was achieved by maintaining the liquid level a few millimeters above the nozzle opening. Drop sizes of 300 μm up to about 700 μm were available at repetition rates up to 50 Hz. However, DOD generation proved to be impractical in the existing furnace due to extreme sensitivity to the height of the liquid level in the reservoir. Also, the liquid tended to bead up around the nozzle, thus preventing drop generation. This problem is easily surmounted by pulsing the reservoir pressure, but without the ability to directly observe the nozzle tip, this solution is impractical. In addition, the low duty cycle of this drop generation mode (~ 50 Hz and less) in comparison to VODG mode (1–15 kHz) made synchronization with the laser and camera very critical. It was very difficult to achieve stable drop generation, proper alignment between the drop stream and the observation volume, and proper synchronization simultaneously. Thus, all experiments were performed in VODG mode.

The drops were injected into the furnace through a specially designed gas/air burner. The gas/air premix entered the combustor via an annulus with an outer diameter of 52.76 mm (2 5/64 in.) and an inner diameter of 42.85 mm (1 11/16 in.). The drop streams were injected through a hole in the center of the annulus and thus through the centerline of both the furnace and the burner. Due to the sensitivity of the piezo-electric elements to heat, the burner was designed to maintain a high flow-rate of cooling water through the head of the burner and around the drop generator nozzle assembly. Even at the maximum heat load attainable, the tip of the aerosol generator was only warm to the touch.

RESULTS AND DISCUSSION

To date, work has focused on the use of filtered full-field images to characterize drop trajectories and sooting behavior. Spectrographic/high resolution data have not been useful for single laser firings, as no atomic or diatomic molecular species present in the reactor absorb and efficiently fluoresce at 308 nm. The $\text{OH}^* \text{X}^2\Pi_i \rightarrow \text{A}^2\Sigma^+$ band overlaps with excimer emission. The band head at 306.36 nm is below the low-wavelength end of the excimer bandwidth, but higher ro-vibronic states overlap portions of the laser spectrum. Typical ro-vibrational Doppler linewidth at 1500 K (the highest temperature obtained from the gas-air flame) is ~ 2 pm. Because

A

B

FIG. 5. PAH fluorescence both in drops and in the atmosphere surrounding drop trajectories.

port of vapor material away from the drop, which will be the subject of future investigation.

At sufficiently high spray rates, drop collisions and coagulation can be seen (Fig. 4). Drop growth as well as vaporization can thus be observed, such that if rogue drops are due to in-flame agglomeration, this will be observable. The fate of diesel drop groups was observed at three points positioned along the centerline of the furnace 12.1 cm, 42.6 cm, and 73.0 cm downstream from the burner. At low gas flow rates, drop groups tended to remain intact even down to the third port, with no coagulation evident. However, as the gas flow was increased, the drop stream was broken up, the drops were observed to form clump like formations, and coagulation was observed at the second and third ports. Except at the highest flow rates, the drop groups were not broken up at the first port. We attribute the breakup of drop formations to turbulence since turbulence is expected near the burner because the Reynold's number within the burner ranged from $Re = 13\,000$ to $Re = 20\,000$, which are clearly in the turbulent regime. The flow was expected to laminarize as the annulus in the burner opened out to the bore of the combustor, where the Reynold's number was calculated to be less than 250. Except at the lowest flow rates, drops were rarely observed at the third port, and these drops no longer remained in linear formation.

A statistical analysis of the coagulation data was only possible for that obtained at the first port due to the limited field of view of the instrument. Given that the active area of the ICCD camera was 12.5×12.5 mm, the 1:1 magnification of the optical system and the laser beam width, the observable volume within the combustor measured $12.5 \text{ mm} \times 12.5 \text{ mm} \times 1.6 \text{ mm}$. As a result, it was difficult to completely characterize drop trajectories ex-

cept at the first port due to drop travel outside the observation volume. However, it was clear that for large drops the paths of the drops were not greatly affected by turbulence until several diameters of the burner annulus downstream.

Another issue of importance for thermal destruction of liquid waste is the gas-phase transport of material originating from the liquid drops and possible uptake by sorbent particles. This was investigated by observing the transport of PAH from diesel drops, as shown in Fig. 5. With the Schott BG-25 and WG-320 filters, the camera was optimized for imaging light in the range of 350 to 450 nm, the emission wavelength range for PAH. The most intense PAH signal arises from the liquid phase, where the strong attenuation of laser light through the thickness of the drops appears as the signal rapidly decays from the right to the left in Fig. 5A. Fluorescence from the gas-phase PAH in a gas-phase concentration map clearly shows the transport of vapor away from the drop array.

Figure 6 shows the radial cross sections of PAH fluorescence from the middle of the drop stream to the edge of the observable volume. The lower curve is the signal through the saddle point between drops, and the upper curve is a cross section through the middle of a drop. The signal through the saddle point decreases in an exponential fashion until it reaches a cusp, which incidentally is where this curve intersects the cross section through the drop. The position of this intersection point does not change with respect to drop injection velocity. This can be explained by the fact that the decay in PAH signal is a combination of diffusive and convective transport away from the drop stream and the thermal degradation of the PAH. Material vaporizing from the drop

to investigate the transport and combustion of materials arising from the drop arrays.

ACKNOWLEDGMENTS

This work was supported in part by the United States Department of Energy Environmental Management Science Program, Grant DE-FG07-97-ER14837. In addition, support from the University of Illinois Research Board is gratefully acknowledged. Fabrication and engineering by and discussion with the University of Illinois School of Chemical Sciences Machine Shop (particularly William Knight, Roger Smith, and Roy Walton), University of Illinois School of Chemical Sciences Electronics Shop, Arne J. Pearlstein, William P. Linak, Sheldon Davis, and Lorenzo Lujan are also greatly appreciated.

1. C. W. Terrell, *Nucl. Mater. Manage.* **23**, 233 (1994).
2. G. Zorpette, *Sci. Am.* **274**(5), 88 (1996).
3. T. L. Stewart, "Overview of U. S. Radioactive Tank Problem," Book of Abstracts, 214th ACS National Meeting, Las Vegas, NV I&EC-055 (1997).
4. S. A. Tollison and S. M. Finger, *Radiat. Prot. Manage.* **14**, 45 (1997).
5. M. L. D. Gougar, B. E. Scheetz, and D. D. Siemer, *Nucl. Technol.* **125**, 93 (1999).
6. S. B. Davis, J. O. L. Wendt, and W. P. Linak, *Chem. Phys. Proc. Combust.* 157 (1999).
7. S. B. Davis, T. K. Gale, and J. O. L. Wendt, *Aerosol Sci. Technol.* **32**, 142 (2000).
8. S. B. Davis and J. O. L. Wendt, *Aerosol Sci. Technol.* **33**, 536 (2000).
9. S. B. Davis and J. O. L. Wendt, *Proc. Combust. Inst.* **28**(Pt. 2), 2743 (2000).
10. J. A. Mulholland, R. K. Srivastava, J. O. L. Wendt, S. R. Agrawal, and W. S. Lanier, *Combust. Flame* **86**, 297 (1991).
11. N. C. Clampitt and G. M. Hieftje, *Anal. Chem.* **44**, 1211 (1972).
12. J. G. Shabushnig and G. M. Hieftje, *Anal. Chim. Acta* **126**, 167 (1981).
13. A. G. Childers and G. M. Hieftje, *Anal. Chem.* **65**, 2761 (1993).
14. A. C. Lazar and P. B. Farnsworth, *Anal. Chem.* **69**, 4932 (1997).
15. J. W. Olesik, *Appl. Spectrosc.* **51**, 158A (1997).
16. J. W. Olesik, J. A. Kinzer, and G. J. McGowan, *Appl. Spectrosc.* **51**, 607 (1997).
17. S. E. Hobbs and J. W. Olesik, *Spectrochim. Acta, Part B* **52**, 353 (1997).
18. I. I. Stewart and J. W. Olesik, *J. Am. Soc. Mass Spectrom.* **10**, 159 (1999).
19. L. A. Melton, *Appl. Opt.* **22**, 2224 (1983).
20. A. M. Murray and L. A. Melton, *Appl. Opt.* **24**, 2783 (1985).
21. H. E. Gossage and L. A. Melton, *Appl. Opt.* **26**, 2256 (1987).
22. S. K. Nickle and L. A. Melton, *Appl. Spectrosc.* **43**, 1406 (1989).
23. L. A. Melton, *Appl. Spectrosc.* **47**, 782 (1993).
24. F. Bai and L. A. Melton, *Appl. Spectrosc.* **51**, 1276 (1997).
25. Q.-Z. Lu and L. A. Melton, *AIAA J.* **38**, 95 (2000).
26. L. A. Melton, *Appl. Opt.* **23**, 2201 (1984).
27. R. T. Wainner, Ph.D. Thesis, Georgia Institute of Technology, Georgia, Atlanta (1999).
28. P. O. Witze, S. Hochgreb, D. Kayes, H. A. Michelsen, and C. R. Shaddix, *Appl. Opt.* **40**, 2443 (2001).
29. S. A. Goldstein and J. P. Walters, *Spectrochim. Acta, Part B* **31**, 201 (1976).
30. R. J. Klueppel, D. M. Coleman, W. S. Eaton, S. A. Goldstein, R. D. Sacks, and J. P. Walters, *Spectrochim. Acta, Part B* **33**, 1 (1978).
31. W. H. Hsu, M. A. Sainz, and D. M. Coleman, *Spectrochim. Acta, Part B* **44**, 109 (1989).
32. A. Scheeline, G. J. Kamla, and M. J. Zoellner, *Spectrochim. Acta, Part B* **39**, 677 (1984).
33. A. Scheeline, C. A. Bye, D. L. Miller, S. W. Rynders, and R. C. Owen, Jr., *Appl. Spectrosc.* **45**, 334 (1991).
34. D. E. Lencioni, *Appl. Phys. Lett.* **23**, 12 (1973).
35. D. E. Lencioni, *Appl. Phys. Lett.* **25**, 15 (1974).
36. J.-B. Zhang, W.-F. Hsieh, S.-C. Chen, and R. K. Chang, *J. Opt. Soc. Am. B* **8**, 319 (1991).
37. J. C. Carls, Y. Seo, and J. R. Brock, *J. Opt. Soc. Am. B* **8**, 329 (1991).
38. M. J. Zoellner and A. Scheeline, *Appl. Spectrosc.* **41**, 943 (1987).
39. T. R. Hanlon and L. A. Melton, *J. Heat Transfer Trans. ASME* **114**, 450 (1992).

**Final Technical Report for
Grant DE-FG07-97ER14837**

**Drop Dynamics and Speciation in Isolation of Metals from
Liquid Wastes by Reactive Scavenging**

**Arne J. Pearlstein
Principal Investigator
Department of Mechanical and Industrial Engineering
University of Illinois at Urbana-Champaign
1206 West Green Street
Urbana, IL 61801
(217) 333-3658
(217) 244-6534 (fax)
ajp@uiuc.edu**

**Alexander Scheeline
Principal Investigator
Department of Chemistry
University of Illinois at Urbana-Champaign
600 South Mathews Avenue
Urbana, IL 61801
(217) 333-2999
(217) 244-8068 (fax)
scheelin@uiuc.edu**

**Final Technical Report for
Grant DE-FG07-97ER14837**

**Drop Dynamics and Speciation in Isolation of Metals from
Liquid Wastes by Reactive Scavenging**

**Arne J. Pearlstein
Principal Investigator
Department of Mechanical and Industrial Engineering
University of Illinois at Urbana-Champaign
1206 West Green Street
Urbana, IL 61801
(217) 333-3658
(217) 244-6534 (fax)
ajp@uiuc.edu**

**Alexander Scheeline
Principal Investigator
Department of Chemistry
University of Illinois at Urbana-Champaign
600 South Mathews Avenue
Urbana, IL 61801
(217) 333-2999
(217) 244-8068 (fax)
scheelin@uiuc.edu**

Summary

During the grant period, we conducted computational and experimental studies of the motion and deformation of liquid drops in gas flows, relevant to the development of high-temperature techniques for isolation of metals from liquid waste.

Computations used the Navier-Stokes equations to predict liquid flow in and gas flow around drops injected into a gas stream. Special attention was focused on the conditions under which drops assume prolate (elongated, "cigar-like") and oblate (flattened, or "pancake-like") shapes. For water drops in air, it is found that the drop shape is spherical if the drop volume is sufficiently small, and then becomes slightly prolate as the drop volume increases. Ultimately, sufficiently large drops are oblate. It is argued that the lack of previous experimental observations of prolate water drops in air is probably due to the presence of surface-active species on the interface, which tend to accumulate at the rear of the drop and greatly reduce the interfacial mobility, thus radically altering the surface pressure distribution and hence the drop shape.

Experimental work focused on the development of spectrometric tools for acquiring laboratory-quality images of drop trajectories and shapes in high-temperature shear flows in harsh, gritty environments. An instrument to accomplish these tasks using emission, fluorescence, and scattering in a 22 kW gas/air combustor was designed, fabricated, and demonstrated. Wavelength dispersion was achieved using a 2.0 m spectrograph f-matched to the feed optics. Images of liquid drops, scattering from soot, and nonaxisymmetric flow in the nominally laminar, axisymmetric combustor were obtained.

Personnel

Principal Investigators

Arne J. Pearlstein, Professor of Mechanical Engineering
Alexander Scheeline, Professor of Chemistry

Postdoctoral Research Associate

Jerry C. Cabalo (present address: US Army Research Laboratory, Aberdeen, Maryland)

Graduate Research Assistant

Min-Po Shiue (present address: Lockheed-Martin Aeronautics Company, Fort Worth, Texas)

Publications

Cabalo, J. C., J. Schmidt, J. O. L. Wendt & A. Scheeline (2002) "Spectrometric System for Characterizing Drop and Powder Trajectories and Chemistry in Reactive Flows," *Applied Spectroscopy*, accepted for publication. (Copy follows)

Shiue, M.-P. and A. J. Pearlstein (2002) "Trajectories and Shapes of Deformable Liquid Drops Undergoing Deceleration in an External Gas Flow," *Combustion and Flame*, to be submitted.

Shiue, M.-P. and A. J. Pearlstein (2002) "Shape, Speed, and Internal Flow of Deformable Water Drops Moving through Air," *Journal of the Atmospheric Sciences*, to be submitted.

Shiue, M.-P. (2001) *Deformation, Acceleration, and Flow of Axisymmetric Drops in Gases at Intermediate Reynolds Numbers*, M.S. Thesis, University of Illinois at Urbana-Champaign. (Copy follows)

**DEFORMATION, FLOW, AND ACCELERATION OF AXISYMMETRIC
DROPS IN GASES AT INTERMEDIATE REYNOLDS NUMBERS**

BY

MINPO SHIUE

B.S., University of Illinois, 1995

THESIS

**Submitted in partial fulfillment of the requirements
for the degree of Master of Science in Aeronautical and Astronautical Engineering
in the Graduate College of the
University of Illinois at Urbana-Champaign, 2001**

Urbana, Illinois

©Copyright by Minpo Shiue, 2001

Abstract

Drop motion in an unbounded gaseous medium is considered computationally.

For steady axisymmetric flow, previous experimental, computational, and approximate analytical work has revealed only oblate drop shapes. Here, we present computational results showing that for a wide range of combinations of the density and viscosity ratios of the continuous and dispersed fluids, there is a range of Reynolds and capillary (or Weber) numbers for which prolate drop shapes are predicted. The transition from oblate to prolate behavior is delineated for water in air and for a model fluid pair considered by Dandy and Leal. If the transition occurs for given density and viscosity ratios, it occurs as Re increases, with the axis ratio passing smoothly through unity without the drop becoming spherical.

We also present computational results for steady axisymmetric flow of water drops through air for a range of drop diameters (100 to 1500 μm) and velocities (0.007 to 27.5 m sec^{-1}). The computed drag coefficients determined for steady axisymmetric drop motion are then used to approximately compute the center-of-mass motion of water drops injected into an air flow parallel to the free stream. This makes use of a nonlinear least-squares fitting of the computed drag coefficients to a predetermined functional form of the Reynolds number. The fitted drag law is then used to integrate the drop trajectories, with the assumption that the drop dynamics are fast compared to the time scale for acceleration or deceleration.

Acknowledgements

I would like to extend my thanks to a few people who helped me along the way. First and foremost, I would like to express my sincerest gratitude to my thesis advisor, Professor Arne Pearlstein for giving me the opportunity and believing in my abilities. Without his guidance and support, I would not be completing a Master of Science degree today.

I would also like to thank Prof Lawrence Bergman for being my academic advisor in the Department of Aeronautical and Astronautical Engineering and for his insight into class selections.

My gratitude also goes out to Lloyd Bozzi and Dr. James Feng for their helpful insight into the finite-element code, and to Professor Ken Beard for information about the UCLA vertical wind tunnel.

I also like to thank my colleagues and friends in 249A MEB: Dr. Lifeng Wang, Dr. Hanjie Lee, Dr. Joe Mantle, David Cotrell, and Florent Petteni.

Lastly, I want to thank my parents for their love, support and encouragement. Without it, I would not be here today

I gratefully acknowledge the support of this work by DOE Grant DE-FG07-97-ER14837.

Table of Contents

	Page
Abstract	iii
Acknowledgements	iv
List of Tables.....	vi
List of Figures	vii
1. Introduction	1
2. Steady Axisymmetric Motion of Deformed Liquid Drops in a Gas	2
2.1. Background	2
2.2. Formulation and Computational Techniques	3
2.2.1. Formulation	3
2.2.2. Computational Method.....	6
2.3. Results	11
2.3.1. Water in Air.....	11
2.3.2. Model Fluid Pair of Dandy and Leal.....	19
2.4. Discussion	21
3. Trajectories of Water Drops Injected into Air	24
3.1. Background	24
3.2. Trajectory Formulation.....	25
3.3. Results	27
4. Conclusion.....	29
References	30

List of Tables

Table	Page
1. <i>Re</i> , computed drag coefficients, "standard" rigid-sphere drag coefficients and axis ratios for water drops in air for $\chi = 8.79 \times 10^3$ and $2r_d = 100 \mu\text{m}$ as a function of drop speed.	33
2. <i>Re</i> , computed drag coefficients, "standard" rigid-sphere drag coefficients and axis ratios for water drops in air for $\chi = 3.52 \times 10^4$ and $2r_d = 400 \mu\text{m}$ as a function of drop speed.	34
3. <i>Re</i> , computed drag coefficients, "standard" rigid-sphere drag coefficients and axis ratios for water drops in air for $\chi = 6.15 \times 10^4$ and $2r_d = 700 \mu\text{m}$ as a function of drop speed.	35
4. <i>Re</i> , computed drag coefficients, "standard" rigid-sphere drag coefficients and axis ratios for water drops in air for $\chi = 1.05 \times 10^5$ and $2r_d = 1200 \mu\text{m}$ as a function of drop speed.	36
5. Reynolds number, axis ratio, dimensionless and dimensional recirculation zone length for falling water drops in air as a function of drop diameters.	37
6. <i>Re</i> , drop velocity, equatorial velocity, and maximum tangential velocity for $2r_d = 710 \mu\text{m}$ at $r_d/r_t = 0.1, 0.2$ and 0.5	38
7. Computed Reynolds number and drag coefficients as a function of drop size and drop velocity, $U < 10 \text{ m sec}^{-1}$	39
8. Computed Reynolds number and drag coefficients as a function of drop size and drop velocity, $U > 10 \text{ m sec}^{-1}$	40
9. Computed Reynolds number and corrected drag coefficients as a function of drop size and drop velocity, $U < 10 \text{ m sec}^{-1}$	41
10. Computed Reynolds number and corrected drag coefficients as a function of drop size and drop velocity, $U > 10 \text{ m sec}^{-1}$	42
11. Least-squares fit of $C_D = A + \frac{B}{Re^{1/2}} + \frac{C}{Re}$ for water drops of different sizes in air. ...	43

List of Figures

Figure	Page
1. Definition sketch.....	44
2a. Typical finite-element mesh of problem domain produced by elliptic mesh generator.	45
2b. Detailed view of the finite element mesh generated by the elliptic mesh generator in and near the drop.	45
3a. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 0.045$, corresponding to $2r_d = 100\mu\text{m}$ at $U = 0.007 \text{ m sec}^{-1}$	46
3b. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 1.94$, corresponding to $2r_d = 100\mu\text{m}$ at $U = 0.30 \text{ m sec}^{-1}$	47
3c. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 3.87$, corresponding to $2r_d = 100\mu\text{m}$ at $U = 0.60 \text{ m sec}^{-1}$	48
3d. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 25.83$, corresponding to $2r_d = 100\mu\text{m}$ at $U = 4.0 \text{ m sec}^{-1}$	49
3e. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 41.98$, corresponding to $2r_d = 100\mu\text{m}$ at $U = 6.5 \text{ m sec}^{-1}$	50
3f. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 64.58$, corresponding to $2r_d = 100\mu\text{m}$ at $U = 10.0 \text{ m sec}^{-1}$	51
3g. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 96.87$, corresponding to $2r_d = 100\mu\text{m}$ at $U = 15.0 \text{ m sec}^{-1}$	52
3h. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 177.59$, corresponding to $2r_d = 100\mu\text{m}$ at $U = 27.5 \text{ m sec}^{-1}$	53

4.	Axis ratio for $\chi = 8.79 \times 10^3$ and $0.045 \leq Re \leq 177.59$, corresponding to $2r_d = 100 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 27.5 \text{ msec}^{-1}$	54
5.	Position of the rear stagnation point, z_{s2} , for $\chi = 8.79 \times 10^3$ and $0.045 \leq Re \leq 177.59$, corresponding to $2r_d = 100 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 27.5 \text{ msec}^{-1}$	55
6	Computed drag coefficients for $\chi = 8.79 \times 10^3$ and $0.045 \leq Re \leq 177.59$, corresponding to $2r_d = 100 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 27.5 \text{ msec}^{-1}$. Solid curve shows "standard" drag curve for rigid sphere.	56
7a.	Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 0.18$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 0.007 \text{ msec}^{-1}$	57
7b.	Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 3.87$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 0.15 \text{ msec}^{-1}$	58
7c.	Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 15.50$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 0.60 \text{ msec}^{-1}$	59
7d.	Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 41.33$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 1.6 \text{ msec}^{-1}$	60
7e.	Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 64.58$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 2.5 \text{ msec}^{-1}$	61
7f.	Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 129.15$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 5.0 \text{ msec}^{-1}$	62
7g.	Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 167.90$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 6.5 \text{ msec}^{-1}$	63
7h.	Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 258.31$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 10.0 \text{ msec}^{-1}$	64

8.	Axis ratio for $\chi = 3.52 \times 10^4$ and $0.18 \leq Re \leq 258.31$, corresponding to $2r_d = 400 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.	65
9.	Position of the rear stagnation point, z_{s2} , for $\chi = 3.52 \times 10^4$ and $0.18 \leq Re \leq 258.31$, corresponding to $2r_d = 400 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.	66
10a.	Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 0.32$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 0.007 \text{ msec}^{-1}$.	67
10b.	Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 27.12$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 0.6 \text{ msec}^{-1}$.	68
10c.	Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 72.33$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 1.6 \text{ msec}^{-1}$.	69
10d.	Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 113.01$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 2.5 \text{ msec}^{-1}$.	70
10e.	Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 226.02$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 5.0 \text{ msec}^{-1}$.	71
10f.	Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 452.04$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 10.0 \text{ msec}^{-1}$.	72
11.	Axis ratio for $\chi = 6.15 \times 10^4$ and $0.32 \leq Re \leq 452.04$, corresponding to $2r_d = 700 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.	73
12.	Position of the rear stagnation point, z_{s2} , for $\chi = 6.15 \times 10^4$ and $0.32 \leq Re \leq 452.04$, corresponding to $2r_d = 700 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.	74
13a.	Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 0.54$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 0.007 \text{ msec}^{-1}$.	75

13b.	Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 23.25$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 0.30 \text{ msec}^{-1}$.	76
13c.	Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 46.49$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 0.60 \text{ msec}^{-1}$.	77
13d.	Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 123.99$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 1.6 \text{ msec}^{-1}$.	78
13e.	Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 193.77$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 2.5 \text{ msec}^{-1}$.	79
13f.	Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 387.47$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 5.0 \text{ msec}^{-1}$.	80
13g.	Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 774.93$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 10.0 \text{ msec}^{-1}$.	81
14.	Axis ratio for $\chi = 1.05 \times 10^5$ and $0.54 \leq Re \leq 774.93$, corresponding to $2r_d = 1200 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.	82
15.	Position of the rear stagnation point, z_{s2} , for $\chi = 1.05 \times 10^5$ and $0.54 \leq Re \leq 774.93$, corresponding to $2r_d = 1200 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.	83
16.	Axis ratio contours for water in air in the $Re-We$ plane. $\diamond \alpha = 1.01$; $\bullet \alpha = 1.001$; $\blacksquare \alpha = 1$; $\blacktriangle \alpha = 0.95$; $\blacktriangledown \alpha = 0.9$; — — falling water drops.	84
17.	Axis ratio contours for water in air in the $Re-Ca$ plane. $\diamond \alpha = 1.01$; $\bullet \alpha = 1.001$; $\blacksquare \alpha = 1$; $\blacktriangle \alpha = 0.95$; $\blacktriangledown \alpha = 0.9$; — — falling water drops.	85
18a.	Terminal velocity of falling water drops in air as a function of drop diameter.	86
18b.	Reynolds numbers of falling water drops in air as a function of drop diameter.	87
19.	Axis ratio for falling water drops in air as a function of drop diameter.	88
20.	Normalized surface area for falling water drops in air as a function of drop diameter.	89

21a.	Equatorial (●) and maximum (■) liquid-side tangential velocities for falling water Drops in air as a function of drop diameter. (♦) indicates the measured value of Pruppacher and Beard (1970) for $2r_d = 710 \mu\text{m}$	90
21b.	Normalized equatorial (●) and maximum (■) tangential velocities for falling water drops in air as a function of drop diameter.	91
22a.	Streamlines and shape of falling water drop in air with $Re = 0.19$ ($2r_d = 50 \mu\text{m}$). ...	92
22b.	Streamlines and shape of falling water drop in air with $Re = 1.46$ ($2r_d = 100 \mu\text{m}$). ..	93
22c.	Streamlines and shape of falling water drop in air with $Re = 8.67$ ($2r_d = 200 \mu\text{m}$). ..	94
22d.	Streamlines and shape of falling water drop in air with $Re = 21.80$ ($2r_d = 300 \mu\text{m}$). ..	95
22e.	Streamlines and shape of falling water drop in air with $Re = 40.52$ ($2r_d = 400 \mu\text{m}$). ..	96
22f.	Streamlines and shape of falling water drop in air with $Re = 64.61$ ($2r_d = 500 \mu\text{m}$). ..	97
22g.	Streamlines and shape of falling water drop in air with $Re = 93.90$ ($2r_d = 600 \mu\text{m}$). ..	98
22h.	Streamlines and shape of falling water drop in air with $Re = 167.93$ ($2r_d = 800 \mu\text{m}$).	99
22i.	Streamlines and shape of falling water drop in air with $Re = 213.00$ ($2r_d = 900 \mu\text{m}$).	100
22j.	Streamlines and shape of falling water drop in air with $Re = 263.99$ ($2r_d = 1000 \mu\text{m}$).	101
22k.	Streamlines and shape of falling water drop in air with $Re = 386.65$ ($2r_d = 1200 \mu\text{m}$).	102
22l.	Streamlines and shape of falling water drop in air with $Re = 544.17$ ($2r_d = 1400 \mu\text{m}$).	103
22m.	Streamlines and shape of falling water drop in air with $Re = 640.07$ ($2r_d = 1500 \mu\text{m}$).	104
23.	Axis ratio as a function of Reynolds number for water drops in air ($2r_d = 100 \mu\text{m}$) at radius ratios $r_d/r_t = 0.1$ (■), 0.2 (●), and 0.5 (▼).	105

24a.	Axis ratio contours for model fluid pair of Dandy and Leal in the $Re-We$ plane. • $\alpha = 1.2$; ■ $\alpha = 1$; ▲ $\alpha = 0.95$; ▼ $\alpha = 0.9$.	106
24b.	Axis ratio contours for model fluid pair of Dandy and Leal in the $Re-Ca$ plane • $\alpha = 1.2$; ■ $\alpha = 1$; ▲ $\alpha = 0.95$; ▼ $\alpha = 0.9$.	107
25a.	Temporal variation of dimensional relative velocities for $2r_d = 100\mu\text{m}$.	108
25b.	Dimensionless temporal variation of velocity ratios for $2r_d = 100\mu\text{m}$.	109
26a.	Temporal variation of dimensional relative velocities for $2r_d = 400\mu\text{m}$.	110
26b.	Dimensionless temporal variation of velocity ratios for $2r_d = 400\mu\text{m}$.	111
27a.	Temporal variation of dimensional relative velocities for $2r_d = 700\mu\text{m}$.	112
27b.	Dimensionless temporal variation of velocity ratios for $2r_d = 700\mu\text{m}$.	113
28a.	Temporal variation of dimensional relative velocities for $2r_d = 1200\mu\text{m}$.	114
28b.	Dimensionless temporal variation of velocity ratios for $2r_d = 1200\mu\text{m}$.	115

1. Introduction

The motion of liquid drops in gases is important in a number of applications. These include scavenging of trace gases and particulate by raindrops falling through the atmosphere, heat and mass transfer from evaporating drops in spray combustion and other high temperature systems, and the parameterization of rainfall events on the basis of radar depolarization.

The present work is motivated by a desire to better understand drop dynamics in high temperature processing systems. In several applications, liquid drops are sprayed into a gas flow, and evaporate or burn. An example is the separation of toxic or radioactive metals from aqueous solution by a process involving volatilization of metal species in a methane flame, followed by scavenging by an inorganic particulate sorbent (Davis, Gale & Wendt 2000; Davis, Gale, Wendt & Linak 2000).

In this and other applications, undesirable emission of species associated with unprocessed liquid (e.g., unburned fuel in spray combustion systems) is largely due to a small number of relatively large "rogue" drops (Wendt, 1994). These drops, which typically result from injector clogging or from variation in liquid properties, are sufficiently large that they either do not follow the streamlines of the flow through the hottest part of the flame (where combustion or evaporation is fastest), or burn or evaporate incompletely in the flame zone (Mulholland et al., 1991). For that reason, it is critical to understand the dynamics of large drops, and in particular how their shapes, internal circulation, and wake affect their aerodynamic behavior.

In Chapter 2, we compute steady axisymmetric internal and external flows and interface shapes for water drops moving through air for a wide range of parameters (Reynolds number and capillary number, Reynolds number and Weber number, or speed and drop diameter). We also present computations for a model fluid pair previously considered by Dandy and Leal (1989). In Chapter 3, we develop simple correlations of drag with drop speed, and use the drag coefficients for water drops in air to compute center-of-mass motion for drops injected into and parallel to an air stream.

2. Steady Axisymmetric Motion of Deformed Liquid Drops in a Gas

2.1. Background

Several previous investigators have reported that axisymmetric liquid drops falling steadily through a second, continuous phase under the action of gravity are oblate (Pruppacher & Beard, 1970), with the axis parallel to the direction of travel being shorter than the perpendicular axis. A single transient computation by Haywood, Renksizbulut, and Ratihby (1994a) for an evaporating heptane drop moving through 10 atm, 100 K air at $Re=100$ and $We=2$ (corresponding to an imposed steady velocity of the drop relative to the air, with Re and We based on initial drop size) shows that after an initial transient period of oblateness, the drop apparently settles into a quasi-steady prolate shape. (The history of the drop until its "endpoint", where evaporation is complete, was not pursued.) These authors proposed that prolate drops had not been observed in previous experimental work due to accumulation of insoluble surface-active material on the drop interface, which reduces the internal circulation in the drop, and hence alters the pressure distribution along the interface. The liquid-side pressure distribution, through the normal stress balance at the interface, influences the variation of interfacial curvature along the interface (Foote, 1969), and hence the drop shape.

To date, however, the only report of prolate axisymmetric drops moving steadily through a viscous medium is the computational work of Bozzi, Mantle, Feng, and Pearlstein (1996), who found that when the dynamic viscosities of the continuous and dispersed phases were equal, there was a minimum density ratio (~ 2.81) below which axisymmetric drops in steady flow are apparently always oblate (for all capillary and Reynolds numbers), and above which prolate drop shapes were possible for some combinations of Ca and Re .

Here, we use a computational approach developed earlier (Bozzi, Feng, Scott & Pearlstein, 1997) and used to study the steady motion and shape of axisymmetric deformable drops moving along the axis of a tube filled with a liquid of the same viscosity and a density either $5/6$ or $6/5$ that of the drop. In most of that work, the ratio of the diameter of an

undeformed drop to the diameter of the tube was 0.5. In the present work for liquid/gas systems, where our interest is in drop behavior in an unbounded domain, we reduce the radius ratio from 0.5 to 0.1, thus reducing the "blockage" by a factor of 25 to 1%. A domain convergence study shows that, at the conditions of interest (primarily determined by Re), the nonzero radius ratio is not a significant issue.

2.2. Formulation and Computational Techniques

2.2.1. Formulation

The formulation and computational approach used to compute the flow are identical to those used in earlier work (Bozzi, 1995; Bozzi et al., 1997). Here, we summarize the important points; the reader is referred to the references for further details.

We consider axisymmetric flow of a liquid drop of volume $4\pi r_d^3/3$ and density ρ_d moving at constant velocity U through an immiscible, otherwise quiescent continuous fluid of density ρ_s . All computations are performed for drops moving axially in a tube of radius r_t , with $r_d/r_t = 0.1$ in the present work. Motion is driven by gravity or another uniform body force aligned with the tube axis and the fluid is motionless far from the drop

The two fluids are taken to be Newtonian and incompressible. The viscosities are denoted by μ_d and μ_c , where subscripts d and c appended to field variables denote quantities associated with the dispersed and continuous fluids, respectively. The interfacial tension, σ , between the fluids is taken to be constant. We select the nonrotating reference frame translating with the drop, and locate the origin of an r - z coordinate system at the center of mass of the drop (Figure 1).

The variables and equations that follow are rendered dimensionless by choosing r_t and U as the characteristic length and velocity, respectively. In each phase, flow is governed by the steady incompressible Navier-Stokes equations internal

$$\frac{\rho_d}{\rho_c} \frac{r_t}{r_d} \frac{Re}{2} \mathbf{u}_d \cdot \nabla \mathbf{u}_d = \nabla \cdot \underline{\mathbf{T}}_d \quad (1a)$$

$$\nabla \cdot \mathbf{u}_d = 0 \quad (1b)$$

and external

$$\frac{r_t}{r_d} \frac{Re}{2} \mathbf{u}_c \cdot \nabla \mathbf{u}_c = \nabla \cdot \mathbf{T}_c \quad (2a)$$

$$\nabla \cdot \mathbf{u}_c = 0 \quad (2b)$$

to the drop. Here, the Reynolds number $Re = 2\rho_c r_d U / \mu_c$ is based on the properties of the continuous fluid and the undeformed drop radius. The stress tensors take the forms

$$\mathbf{T}_d = -\Pi_d \mathbf{I} + \frac{\mu_d}{\mu_c} [\nabla \mathbf{u}_d + (\nabla \mathbf{u}_d)^T] \quad (3a)$$

and

$$\mathbf{T}_c = -\Pi_c \mathbf{I} + [\nabla \mathbf{u}_c + (\nabla \mathbf{u}_c)^T], \quad (3b)$$

where $\Pi_j = (p_j - \rho_j g z) / (\mu_c U / r_t)$ ($j = d, c$) is the dimensionless pressure in phase j , and $\mathbf{I}$ is the identity tensor. The stress and pressure are measured in units of $\mu_c U / r_t$. In cylindrical coordinates, the axisymmetric swirl-free velocity fields $\mathbf{u}_d$ and $\mathbf{u}_c$ have components $(u_d, 0, w_d)$ and $(u_c, 0, w_c)$, respectively, in the r -, ϕ -, and z -directions.

At the fluid/fluid interface, conservation of momentum is expressed by the traction boundary condition

$$\mathbf{n} \cdot (\mathbf{T}_c - \mathbf{T}_d) = \frac{1}{Ca} \left[\frac{d\mathbf{t}}{ds} + \frac{\mathbf{n}}{r} \frac{dz}{ds} \right] - \mathbf{n} St (r_t / r_d)^2 z \quad (4)$$

on the surface S_d . Here, $Ca = \mu_c U / \sigma$ is the capillary number, $St = (\rho_d - \rho_c) g r_d^2 / (\mu_c U)$ is a dimensionless buoyancy force, $\mathbf{n}$ and $\mathbf{t}$ are the local unit normal and tangent vectors to the interface, and s is the arclength along the interface, measured from the forward stagnation point. We take $\mathbf{n}$ to be directed into the drop and $\mathbf{t}$ to be in the direction of increasing s , so that the second factor of the first term on the right-hand side of (4) is the sum of the local mean curvatures. The interface is a material surface, provided no mass transfer occurs across it; its shape is unknown *a priori*. For steady flow, the kinematic conditions at the drop interface S_d are

$$\mathbf{n} \cdot \mathbf{u}_d = 0 \quad (5a)$$

and

$$\mathbf{n} \cdot \mathbf{u}_c = 0 \quad (5b)$$

On this surface, the velocity is continuous

$$\mathbf{u}_c = \mathbf{u}_d \quad (6)$$

At the tube wall ($r=1$), the continuous fluid moves relative to the drop and satisfies the no-slip and no-penetration conditions, viz.

$$\mathbf{u}_c = \mathbf{e}_z \quad (7)$$

where $\mathbf{e}_z$ is the unit vector in the z -direction. The velocity asymptotically approaches a uniform flow

$$\mathbf{u}_c \rightarrow \mathbf{e}_z \quad (8)$$

as $|z| \rightarrow \infty$.

Along the axis of symmetry ($r=0$), we impose the conditions

$$\mathbf{e}_z \mathbf{e}_r : \underline{\underline{\mathbf{T}}}_c = 0 \quad (9a)$$

$$u_c = 0 \quad (9b)$$

$$\mathbf{e}_z \mathbf{e}_r : \underline{\underline{\mathbf{T}}}_d = 0 \quad (9c)$$

and

$$u_d = 0 \quad (9d)$$

where $\mathbf{e}_r$ is the unit vector in the r -direction.

Equations (1-9) involve the six independent dimensionless parameters Re , Ca , r_d/r_t , ρ_d/ρ_c , μ_d/μ_c , and St . An alternate set is Re , Ca , r_d/r_t , ρ_d/ρ_c , μ_d/μ_c , St , and $\chi = 2r_d\sigma/(\rho_d v_d^2)$. Specification of any five fixes the sixth. In physical terms, we see that fixing the geometry, fluid properties, and gravitational acceleration will determine the terminal velocity of the drop. Alternatively, if the terminal velocity, geometry, and fluid properties are specified, then the buoyancy force must balance the drag on the drop, and g is thus determined.

For the present purpose, it is convenient to specify Re , Ca , r_d/r_t , ρ_d/ρ_c , and, μ_d/μ_c and to require that the drop center-of-mass remains at the origin

$$z_{cm} = \iiint_V z dV = \int_{s_1}^{s_2} z \pi r^2 \frac{dz}{ds} ds = 0 \quad (10)$$

Thus, St is an unknown determined as part of the solution.

2.2.2. Computational Method

The free-boundary problem (1-10) is solved on the domain including the deformable interface separating the drop and the continuous fluid, using a Galerkin finite-element method implemented in a code developed by Bozzi et al. (1997), based on an earlier code of Scriven and coworkers (Kistler & Scriven 1983; Christodoulou & Scriven 1989; Christodoulou 1990; de Santos 1991).

The domain is subdivided into a set of quadrilateral elements (cf. Strang & Fix 1973), each of which is mapped onto a unit square. On each unit square, the unknown velocity and pressure fields are represented by an expansion in biquadratic and linear basis functions, respectively. That is, the discretization is performed in the mixed interpolation sense (Huyakorn et al. 1978) to avoid over-constraint problems. To facilitate simultaneous determination of the flow and interface shape, an elliptic mesh generation scheme (Thompson, Warsi & Mastin 1985) developed by Christodoulou and Scriven (1992) and modified by de Santos (1991) is employed. The essence of the method is to determine the locations of the nodal or mesh points of a finite-element grid by solving a pair of elliptic partial differential equations

$$\nabla \cdot D_\xi \nabla \xi = 0 \quad (11a)$$

and

$$\nabla \cdot D_\eta \nabla \eta = 0 \quad , \quad (11b)$$

where the "diffusion" coefficients D_ξ and D_η are adjustable functions of position prescribed to meet particular requirements for the distribution of nodal or mesh points in the domain. The computational burden of solving the mesh generation equations (11a,b) is reduced by using the subparametric nodal position mapping described by Christodoulou and Scriven (1992), instead of the isoparametric mapping commonly used in finite-element computations. The mesh is determined concomitantly with the flow (see below), allowing the "origin" of the finite-element mesh to vary relative to the center of mass.

Inflow and outflow boundary conditions replacing (8) are imposed a finite distance upstream and downstream of the drop. At the inflow boundary S_{in} , a Dirichlet condition analogous to (8) is specified for $0 \leq r \leq 1$. At the outflow boundary S_{out} , the Neumann and Dirichlet conditions

$$\mathbf{n} \cdot \nabla \mathbf{u}_c = 0 \quad , \quad (12a)$$

$$\mathbf{t} \cdot \mathbf{u}_c = 0 \quad , \quad (12b)$$

and

$$\Pi = 0 \quad , \quad (12c)$$

are imposed on the z - and r -components of velocity, and the pressure.

To eliminate variations in drop volume associated with discretization and other sources of numerical error, we also impose a volume constraint

$$\int_{s_1}^{s_2} \pi r^2 \frac{dz}{ds} = \frac{4}{3} \pi (r_d/r_t)^3 \quad , \quad (13)$$

which requires an additional degree of freedom in the mathematical system. This is obtained by specifying a reference pressure, independent of (12c), at a point inside the drop. Since specifying the pressure at any node in the domain determines (through the partial differential equations and boundary conditions) the pressure field in the entire domain, specifying the pressure independently inside and outside the drop requires introduction of an undetermined "correction factor" $\Delta \Pi_0$ to the pressure jump across the drop interface. Numerically, this is

accomplished by replacing one of the discretized field equations at one point in the drop by an essential condition for pressure, and by introducing the additive term $\Delta\pi_0$ in the normal stress boundary condition. The net effect is to add one equation (13) and one additional unknown ($\Delta\pi_0$), leaving the system well-posed.

The Galerkin finite-element statement of the problem is completed by imposing boundary conditions on the mesh generation equations (11a,b). Along the drop interface and boundaries parallel to it in the computational domain, equal arclength spacing of grid points is enforced by Dirichlet conditions on the relevant mesh generation equations. On boundaries perpendicular to the interface in the computational domain, Dirichlet conditions are imposed with nonuniform D_ξ or D_η defined in a piecewise fashion (Eiseman 1982a,b; Thompson, Warsi & Mastin 1982, 1985; de Santos 1991; Christodoulou & Scriven 1992), so that grid points are compressed toward the interface where additional resolution is anticipated to be most useful.

Once the mathematical system is completely described, the nodal values and nodal locations are represented in the mixed interpolation scheme

$$\mathbf{u} = \sum_i \mathbf{u}_i \phi^i(\xi, \eta) \quad , \quad (14)$$

$$\pi = \sum_k \pi_k \psi^k(\xi, \eta) \quad , \quad (15)$$

and

$$\mathbf{x} = \sum_l \mathbf{x}_l \theta^l(\xi, \eta) \quad . \quad (16)$$

Here, ϕ^i and ψ^k are the biquadratic and linear discontinuous basis functions in the (ξ, η) domain, respectively, $\mathbf{x}_l$ are the nodal locations, and θ^l is the subparametric mapping function (cf. Christodoulou & Scriven 1992). Galerkin's method is applied by weighting the governing equations (1a,2a) with ϕ^i , (1b,2b) with ψ^k , and (11a,b) with θ^l . The weighted equations are then integrated over the entire physical domain to obtain

$$\mathbf{R}_i^M \equiv \int_A \left[(B\mathbf{u} \cdot \nabla \mathbf{u}) \phi^i + \nabla \phi^i \cdot \underline{\mathbf{T}} \right] dA - \int_{\partial A} \mathbf{n} \cdot \underline{\mathbf{T}} \phi^i ds = 0 \quad , \quad (17)$$

$$R_k^C \equiv \int_A \psi^k \nabla \cdot \mathbf{u} dA = 0 , \quad (18)$$

$$R_l^{G,\xi} \equiv \int_A \nabla \theta^l \cdot (D_\xi \nabla \xi) dA - \int_{\partial A} \mathbf{n} \cdot (D_\xi \nabla \xi) \theta^l ds = 0 , \quad (19a)$$

and

$$R_l^{G,\eta} \equiv \int_A \nabla \theta^l \cdot (D_\eta \nabla \eta) dA - \int_{\partial A} \mathbf{n} \cdot (D_\eta \nabla \eta) \theta^l ds = 0 , \quad (19b)$$

for the residuals, where B is the "phase-dependent" coefficient of the nonlinear term in (1a) or (2a), and superscripts M , C , and G refer to momentum, continuity, and mesh generation, respectively. Dirichlet conditions are prescribed by replacing the appropriate residual equation with an essential boundary condition (cf. Kistler & Scriven 1983). Neumann boundary conditions are enforced through the surface integrals in (17) and (19a,b). We form residuals for the position constraint (10)

$$R^F \equiv \int_{s_1}^{s_2} z \pi r^2 \frac{dz}{ds} ds = 0 , \quad (20)$$

and volume constraint (13)

$$R^V \equiv \int_{s_1}^{s_2} \pi r^2 \frac{dz}{ds} ds - \frac{4}{3} \pi (r_d / r_t)^3 = 0 . \quad (21)$$

Equation (17) symbolically represents two equations on each element in the interior of the domain, A , while (18-19) each represent a single equation on each element, and (20-21) are single equations. The divergence theorem was used to lower the order of derivatives in the discretized momentum and mesh generation equations. The system (17-21) constitutes a finite set of nonlinear algebraic equations which can be written in summary form as

$$\mathbf{R}(\{z_i\}, \{r_i\}, \{u_i\}, \{w_i\}, \{\Pi_0\}, St, \Delta \Pi_0) = \mathbf{R}(\mathbf{q}) = \mathbf{0} . \quad (22)$$

Here, $\{z_i\}$ and $\{r_i\}$ are the nodal position unknowns determined by the elliptic mesh generation equations (11a,b), $\{u_i\}$ and $\{w_i\}$ are the nodal values of the r - and z -components of velocity,

and $\{II_i\}$ are the nodal values of pressure. The vector $\mathbf{q}$ includes all nodal unknowns, in addition to St and $\Delta\Pi_0$. The system (22) is solved by Newton's method

$$\underline{\underline{\mathbf{J}}}^{(k)} \Delta \mathbf{q}^{(k+1)} = -\mathbf{R}^{(k)} \quad (23)$$

In (23), $\underline{\underline{\mathbf{J}}} = \partial \mathbf{R} / \partial \mathbf{q}$ is the Jacobian matrix of partial derivatives, $\Delta \mathbf{q}^{(k+1)} = \mathbf{q}^{(k+1)} - \mathbf{q}^{(k)}$, and k denotes the k -th iterate. At each Newton iteration, the linear system (23) is solved by direct factorization or LU-decomposition of the Jacobian using a modification of Hood's frontal solver (Hood 1976; Walters 1980).

Critical to Newton's method is a sufficiently accurate initial iterate. A convenient initial iterate is obtained by solving the governing equations for Stokes flow ($Re = 0$) and small capillary number, e.g., $Ca = 0.005$ (equivalently, high interfacial tension), for which the drop shape is well-approximated by a sphere. Thereafter, steady solution families can be traced efficiently by first-order continuation (Riks 1972; Keller 1977) either in Re , holding Ca fixed, or in Ca , holding Re fixed.

Inlet and outlet boundaries are located at $z = -5$ and $z = 10$, so that imposition of boundary conditions (8) and (12) a finite distance from the drop has virtually no effect on the solutions. Figures 2(a,b) show a typical mesh of 727 elements. For each such mesh, the number of velocity, pressure, and nodal position unknowns is 6074, 2247, and 3037, respectively, and the interface is discretized into 40 adjacent segments, each corresponding to the common edge of one element in the drop and one outside, giving 81 interfacial nodes. For the meshes used, as typified by those shown in Figure 2, elements at the origin appear triangular, and are implemented in our code as regular quadrilateral elements, for which two adjacent vertices coincide in the physical domain. Typically, five Newton iterations suffice to bring the L_2 norm of the residuals and the error in the solution below 10^{-5} . For water drops with diameter $2r_d = 1200 \mu\text{m}$ in air (a highly deformed case), decreasing the number of elements by 200 changes the drag coefficient by less than 2% for $Re = 774.9$, $Ca = 0.002621$. For less deformed

drops, the fractional change is considerably less. Unless otherwise indicated, Newton iteration always converged, with no hint of singularity in the Jacobian.

The code was validated by Bozzi, Feng, Scott & Pearlstein (1997) by comparison to previous work, including the classic experimental work of Winnikow and Chao (1966) and the computational work of Dandy and Leal (1989), both in an unbounded domain, and Stokes flow calculations of Haberman and Sayre (1958) and Coutanceau and Thizon (1981) for an undeformed drop falling in a vertical tube.

2.3. Results

2.3.1. Water in Air

The formulation described in the previous section involves five independently specifiable dimensionless parameters, namely Re , Ca , r_d/r_i , ρ_d/ρ_c , and μ_d/μ_c . We consider two cases. For water drops in air ($\mu_d/\mu_c = 48.55$ and $\rho_d/\rho_c = 841.44$), we present results over the ranges $0 < Re < 800$ and $1.84 \times 10^{-6} \leq Ca \leq 7.21 \times 10^{-3}$, corresponding to $100 \mu\text{m} \leq 2r_d \leq 1200 \mu\text{m}$ and $0.007 \text{ msec}^{-1} \leq U \leq 10 \text{ msec}^{-1}$. We also consider the flow for the property value ratios of a model fluid pair considered by Dandy and Leal ($\mu_d/\mu_c = 100$, $\rho_d/\rho_c = 1000$), over the ranges $0 < Re < 4000$ and $0 < Ca < 0.6$.

In what follows, we present the computed streamlines, axis ratio α , drag coefficient C_D , and position of the rear stagnation point of the recirculation zone relative to the rear of the drop, z_{s2} , as functions of Re for several fixed values of the dimensionless parameter $\chi = 2r_d\sigma/(\rho_d v_d^2)$, which for water and air or any other fluid pair, depends only on undeformed drop diameter. The streamlines are level curves of $dr/u = dz/w$ and the motion of the drop is depicted as a flow from left to right past a fixed drop. We define the drag coefficient as

$$C_D = \frac{\frac{4}{3}\pi r_d^3 |\rho_c - \rho_d| g}{\frac{1}{2}\rho_c U^2 \pi r_d^2}, \quad (24)$$

and the axis ratio as

$$\alpha = 2r_{\max} / \Delta z_{\max} , \quad (25)$$

where $r_{\max}$ and $\Delta z_{\max}$ are the maximum radial and axial extents of the drop. We frequently indicate the value of the Weber number, $We = ReCa$, which is determined (like Re) by the size and speed of the drop.

We note that although a spherical drop necessarily has an axis ratio of unity, a drop with $\alpha = 1$ is not necessarily spherical, as discussed previously by Bozzi et al. (1997). Another measure of sphericity is the normalized surface area, defined as

$$A_{\text{surface}} = \frac{1}{4\pi(r_d/r_t)^2} \int_{s_1}^{s_2} 2\pi r \, ds , \quad (26)$$

which is equal to unity only for spherical drops.

We begin with a discussion of the effect of Re on flow and drop shape, focusing on three different ranges of χ . In each case, the corresponding dimensional drop sizes and speeds are also given. For each value of χ , we start with a small relative velocity, $U_o = 0.007 \text{ m sec}^{-1}$ ($Re \ll 1$, for all cases) and increase Re until well past the point where transition from oblate ($\alpha > 1$) to prolate drop ($\alpha < 1$) behavior occurs.

Small Drops. We begin with small drops ($\chi = 8.79 \times 10^3$), corresponding to $2r_d = 100 \, \mu\text{m}$, for which we show the streamlines (Figures 3(a-h)) and axis ratio (Figure 4) for $0 < Re < 180$ (U up to 27.5 m sec^{-1} , and We up to 7.21×10^{-3}). At $Re = 0.045$ ($U = 0.007 \text{ m sec}^{-1}$; Figure 3a), the drop and the flow in and past it are essentially fore-aft symmetric, and α is nearly unity. By $Re = 1.94$ ($U = 0.30 \text{ m sec}^{-1}$; Figure 3b), the flow past the drop is visibly asymmetric, although the drop and internal flow are still almost spherical and symmetric, respectively. As Re increases, the computed axis ratio differs from unity by less than one part in 10,000 up to $Re = 3.87$ ($U = 0.6 \text{ m sec}^{-1}$; Figure 3c). As Re increases, the flow inside the drop becomes visibly fore-aft asymmetric ($Re = 25.83$, corresponding to $U = 4.0 \text{ m sec}^{-1}$; Figure 3d). By $Re = 41.98$ ($U = 6.5 \text{ m sec}^{-1}$; Figure 3e), a significant

recirculation zone has developed in the wake of the drop. As Re increases, the recirculation region continues to grow, reaching an axial extent in excess of one-half the drop length by $Re = 64.58$ ($U = 10.0 \text{ msec}^{-1}$; Figure 3f). As Re increases further, the drop becomes more oblate, reaching a maximum axis ratio ($\alpha = 1.009$) near $Re = 97$ (15 msec^{-1} ; Figure 3g). Figure 3h shows that by $Re = 177.59$ (27.5 msec^{-1} ; Figure 3h) the recirculation zone is visibly longer than the drop and has nearly the same radial extent. The computations have not been extended significantly past this Reynolds number since experimental evidence suggests that bluff-body flows, including flows past liquid drops, then to become unstable as the wake diameter approaches the "body" diameter. Figure 4 shows that the drop is prolate at this highest Re , with axis ratio 0.987.

Figure 5 shows that the location of the end of the recirculation zone relative to the rear stagnation point of the drop, z_{s2} , increases rapidly with Re above the Reynolds number (~ 28.0) at which recirculation first occurs. The recirculation zone remains attached to the drop at all Reynolds numbers considered. The length of this zone increases with Reynolds number approximately like $(Re - Re_{sep})^n$ where $Re_{sep} \approx 28.0$ is the Reynolds number at which the recirculation zone first appears, and $0 < n < 1$. This rapid growth differs from the case of a rigid sphere (Kim 1989; Mantle 2000), for which the growth is initially linear. Figure 6 shows the computed drag coefficient for $\chi = 8.79 \times 10^3$ ($2r_d = 100 \mu\text{m}$) as a function of Reynolds number in the range $0.045 \leq Re \leq 177.59$ (corresponding to $0.007 \text{ msec}^{-1} \leq U \leq 27.5 \text{ msec}^{-1}$), along with the so-called "standard" drag curve for a rigid sphere (Clift, Grace, and Weber, 1978, Table 5.2). As expected on the basis of interfacial "slip," the computed drag coefficients do not exceed the rigid-sphere values. Numerical values of the computed and rigid-sphere drag coefficients, and computed axis ratios, are shown in Table 1.

Medium-Size Drops. For $\chi = 3.52 \times 10^4$ ($2r_d = 400 \mu\text{m}$), Figures 7(a-h) show the development of the flow field as a function of Reynolds number. The results are qualitatively similar to the $\chi = 8.79 \times 10^3$ ($2r_d = 100 \mu\text{m}$) case with fore-aft asymmetry becoming apparent in the exterior and interior flows by $Re = 3.87$ ($U = 0.15 \text{ msec}^{-1}$; Figure 7b) and $Re = 15.50$

($U = 0.60 \text{ msec}^{-1}$; Figure 7c), respectively. At $Re = 41.33$, ($U = 1.6 \text{ msec}^{-1}$; Figure 7d), a recirculation zone has appeared, which grows axially and radially for all Re considered. At $Re = 258.31$ ($U = 10.0 \text{ msec}^{-1}$; Figure 7h), the radial extent of the recirculation zone is approximately equal to that of the drop, to which it attaches at a radius not much less than that of the drop. Note that although the Reynolds number for this drop exceeds that for which flow past a rigid sphere is thought to become nonaxisymmetric and soon thereafter unsteady (Johnson and Patel, 1999), we have included it because motion of liquid drops without adsorbed surfactant is known to be axisymmetric and steady up to Reynolds numbers well beyond 800 (Winnikow and Chao, 1966).

Figure 8 shows that α is nearly unity up to about $Re = 3.9$ ($U = 0.015 \text{ msec}^{-1}$). Like the smaller drop ($\chi = 8.79 \times 10^3$) discussed above, the drop shape become increasingly oblate with increasing Re , reaching a maximum ($\alpha = 1.0002$) around $Re = 100$ (3.9 msec^{-1}). We note that the maximum α here is about 1.00025 (Figure 8), compared to 1.009 for the smaller drop (Figure 4). By $Re = 167.90$ ($U = 6.5 \text{ msec}^{-1}$; Figure 7g), the drop shape has changed from oblate to prolate.

Figure 9 shows that the recirculation zone appears at a Reynolds number similar to that for the smaller drop. The Re dependence of z_{s2} is very similar to that computed for $\chi = 8.79 \times 10^3$ ($2r_d = 100 \mu\text{m}$; Figure 5). Numerical values of the computed and rigid-sphere drag coefficients, and computed axis ratios, are shown in Table 2.

Large Drops. Here, we present results for two larger values of χ . Figures 10(a-f) show streamlines and drop shape as a function of Re for $\chi = 6.15 \times 10^4$ ($2r_d = 700 \mu\text{m}$), for $0 < Re < 460$ ($U \leq 10.0 \text{ m sec}^{-1}$) and $We \leq 1.185$. The development of the drop shape and flow with Re is quite similar to that predicted for the smaller drops discussed above, except as noted below. Fore-aft asymmetry of the streamlines can be discerned even at the smallest Re of 0.32 (0.007 msec^{-1} ; Figure 10a), although the drop shape and internal flow are essentially symmetric. Figure 11 shows that the axis ratio initially increases slightly with Re , reaching a maximum of approximately 1.0012 near $Re = 113$ ($U = 2.5 \text{ msec}^{-1}$; Figure 10d). By

$Re = 180.82$ ($U = 4.0 \text{ msec}^{-1}$), the drop becomes significantly prolate ($\alpha = 0.91$) at $Re = 452.04$ (10 msec^{-1}).

Figure 12 shows the dependence of z_{s2} on Reynolds number for $0 < Re \leq 452.04$ ($U = 0.007 \text{ msec}^{-1}$). As for the smaller drops, z_{s2} appears to grow like $(Re - Re_{sep})^n$ initially. In this case, however, the computed length of the recirculation zone (normalized with r_d) appears to reach an asymptotic value of ~ 3.4 at a Reynolds number of about 400. This result might be an attribute of the flow in an unbounded domain, or might be an artifact of the finite tube size $r_d/r_t = 0.1$ employed in the computations. Numerical values of the computed and rigid-sphere drag coefficients, and computed axis ratios, are shown in Table 3.

For even larger drops, Figures 13(a-g) show the evolution of the flow and drop shape for the largest drop $\chi = 1.05 \times 10^5$ ($2r_d = 1200 \mu\text{m}$) considered in this study. The development of flow with increasing Reynolds number is quite similar to the smaller drops with several notable exceptions. First, at $Re = 387.47$ ($U = 5.0 \text{ msec}^{-1}$; Figure 13f) the radial extent of the recirculation zone exceeds that of the drop. Second, at $Re = 774.93$ ($U = 10.0 \text{ msec}^{-1}$; Figure 13g), the drop is quite prolate.

Figure 14 shows that the axis ratio remains nearly unity up to a Reynolds number about 200 and then decreases perceptibly, passing through 0.9 near $Re = 550$ and reaching 0.787 at $Re = 774.93$.

Figure 15 shows a dependence of z_{s2} on Re quite similar to those found for smaller drops, except that the computed length of the recirculation zone decreases slightly with Re beyond 500. Again, whether this result is an attribute of the real unbounded flow or an artifact of the finite tube size is unclear. Numerical values of the computed and rigid-sphere drag coefficients, and computed axis ratios, are shown in Table 4.

Constant Axis Ratio Contours. In Figure 16, we show contours of constant axis ratio in the two-dimensional $Re-We$ plane for water drops in air. The $\alpha = 1$ contour is nearly horizontal ($Re \approx 150$) over the entire range of We considered, and has a limit point on the $We = 0$ axis, on which α must be unity, since there is no deformation as $\sigma \rightarrow \infty$ or $U \rightarrow 0$.

For prolate drops ($\alpha < 1$), the contours appear to have a vertical asymptote, although it is unclear whether the asymptote is at $We = 0$ or a nonzero We . For the two prolate contours shown ($\alpha = 0.9$ and 0.95), the results suggest the $We = 0$ axis and Re horizontal asymptote of the $\alpha = 1$ contour (hereinafter referred to as $Re_{\alpha=1}$) as the vertical and horizontal asymptotes, respectively. For oblate drops ($\alpha > 1$), a horizontal asymptote at $Re_{\alpha=1}$ is apparent.

In Figure 17, we show the constant- α contours in the Re - Ca plane. The $\alpha = 1$ contour is again essentially horizontal ($Re \approx 150$) and has a limit point on the $Ca = 0$ axis. For prolate drops, the contours again suggest the existence of both vertical and horizontal asymptotes, with the vertical and horizontal asymptotes at $Ca = 0$ and $Re_{\alpha=1}$, respectively.

For oblate drops ($\alpha > 1$), two horizontal asymptotes are apparent at $Re_{\alpha=1}$ and 0 . For $\alpha = 1.001$ and 1.01 the turning points are near $Ca = 3 \times 10^{-4}$ and $Ca = 3 \times 10^{-3}$, respectively.

Falling Drops. Figures 16 and 17 also show the Re - We and Re - Ca relationships for water drops falling in air at normal gravity. In both cases, the curve begins with a small drop near the origin and extends to $2r_d = 1500 \mu\text{m}$ at the high Re , high We or high Re , high Ca terminus. Falling drops are seen to be oblate if sufficiently small ($Re < 150$ or $2r_d < 750 \mu\text{m}$), and become prolate beyond that point. Note that solutions of the Navier-Stokes equations are anti-symmetric in z with respect to a sign change in the velocity, corresponding to changing the signs of Re and Ca , or of Re alone in an Re - We formulation. Thus, the 1-g curve passes through the origin in the Re - Ca plane, and could be extended into the third quadrant of the Re - Ca plane (corresponding to reversing the direction of the gravitational acceleration).

Figures 18(a,b) show the dependence of the dimensional terminal velocity and Reynolds number, respectively, on drop diameter up to $2r_d = 1500 \mu\text{m}$. The dependence of the terminal velocity on diameter is nearly linear over a wide range, becoming perceptibly superlinear only at drop sizes above $1000 \mu\text{m}$. The dependence of Reynolds number on diameter is strongly superlinear beginning with the smallest drop. Both curves are in excellent agreement with the standard 1 atm curve of Beard (1976).

Figure 19 and Table 5 show that the axis ratio initially increases to values slightly above unity as the drop diameter increases, consistent with the results of Pruppacher and Pitter (1971) in the UCLA vertical wind tunnel. The computed axis ratio reaches a maximum near $Re = 94$, after which it decreases, passes through unity. For still larger diameters, the drop is prolate. For example, $\alpha = 0.988$ for a $1000 \mu\text{m}$ drop ($Re = 263.98$). On the other hand, the experimental results of Pruppacher and Pitter (1971) and other investigations in the UCLA vertical wind tunnel cited therein show that suspended drops become increasingly oblate as the drop diameter increases. This discrepancy and a proposed explanation for it are discussed in more detail in §2.4.

Figure 20 shows that the surface area of a water drop falling in air is indistinguishable from that of an undeformed drop for $2r_d < 1000 \mu\text{m}$, and increases rapidly for larger drops. This result shows that, while the normalized surface area is a less ambiguous measure of departures from sphericity than the axis ratio, it is also considerably less sensitive.

Figure 21a shows how the equatorial and maximum values of the tangential liquid velocity depend on drop size for falling drops. Note that the maximum velocity need not occur on the equator (defined for an arbitrarily deformed drop as the point farthest from the axis), and typically occurs slightly upstream of the equator. Both the equatorial and maximum values of the tangential velocity increase monotonically with drop size. For small drops ($2r_d < 200 \mu\text{m}$), the maximum and equatorial tangential velocities are essentially equal. For larger drops, the maximum tangential velocity is sensibly higher than the equatorial velocity.

Figure 21b shows that the equatorial and maximum tangential velocities, both normalized by the center-of-mass velocity, approach an identical value (given by the well-known Rybczynski-Hadamard theory; cf. Clift et al. 1978 and Lamb 1932) at small drop sizes, corresponding to spherical drops. As the drop size increases, the normalized maximum tangential velocity becomes larger than its equatorial counterpart, with the relative difference reaching a maximum value of about 15% at $2r_d = 600 \mu\text{m}$. Beyond that point, the relative difference between the equatorial and maximum values decreases, while both tangential

velocities increase less rapidly with increasing drop diameter. At $2r_d = 1500 \mu\text{m}$, both tangential velocities are about $0.065 U$.

As discussed above, Figure 19 and Table 5 show that the axis ratio remains very close to unity until $2r_d \sim 800 \mu\text{m}$, beyond which α decreases rapidly with increasing drop size. Figures 22(a-m) show the development of the internal and external flow for water drops falling in air as a function of drop size. We note that the radial extent of the recirculation region increases until reaching approximately that of the (deformed) drop. The internal flow initially becomes more fore-aft asymmetric as drop size increases. Beyond about $2r_d \sim 500 \mu\text{m}$, however, the degree of asymmetry in the internal flow decreases until $2r_d \sim 1000 \mu\text{m}$. From that drop size up to $2r_d = 1500 \mu\text{m}$, the only discernible fore-aft asymmetry in the internal flow is seen in a small region near the rear stagnation point.

The recirculation zone first appears between 300 and $400 \mu\text{m}$. Table 5 shows both its dimensionless extent, z_{s2} , as well as the dimensional extent $r_d z_{s2}$. Both quantities increase monotonically with drop size until $2r_d \sim 1400 \mu\text{m}$, beyond which the dimensionless axial extent of the recirculation zone decreases while the dimensional extent continues to increase. This situation differs from that shown for $\chi = 1.05 \times 10^5$ ($2r_d = 1200 \mu\text{m}$), for which both the dimensionless (and dimensional) axial extents both decreased beyond $Re = 500$.

Wall effects. We continue with a discussion of wall effects on the computed values of α . Figure 23 shows the dependence of α on Re for $\chi = 8.79 \times 10^3$ ($2r_d = 100 \mu\text{m}$) at three different values of r_d/r_t . We note that in each case, the initial deformation of the drop is oblate. For $r_d/r_t = 0.1$ and 0.5 , axis ratios computed at $Re = 2 \times 10^{-4}$ are 1.0003 and 0.9990, respectively. Note that at $Re = 0$, a liquid drop in an unbounded gaseous medium (with $\rho_d/\rho_c > 53.125$) is expected to be oblate, as shown by the theoretical work of Taylor and Acrivos (1964). As shown by Bozzi et al. (1997), however, drops moving axisymmetrically through a tube at $r_d/r_t = 0.5$ with $Re \ll 1$ are slightly prolate. This is clearly an effect of the proximity of the tube wall, as evidenced by the oblate-to-prolate transition we find between $r_d/r_t = 0.5$ and $r_d/r_t = 0.1$ at $Re = 2 \times 10^{-4}$ described above.

For $r_d/r_t = 0.5$, the axis ratio reaches a maximum value of about 1.003 near $Re = 48$. The axis ratio then decreases, with the drop becoming prolate near $Re = 75$. Beyond that point, the reduction in α is quite steep, with the axis ratio falling to 0.95 by $Re = 145$ and to 0.9 near $Re = 180$. As r_d/r_t decreases, Figure 23 shows that the maximum degree of oblateness increases, with α attaining maximum values of 1.008 and 1.009 for $r_d/r_t = 0.2$ and $r_d/r_t = 0.1$, respectively, both near $Re = 96$. As in the $r_d/r_t = 0.5$ case, α then decreases, passing through unity near 145 and 155 for $r_d/r_t = 0.2$ and 0.1, respectively.

We note that when the "blockage" is reduced from 25% (at $r_d/r_t = 0.5$) to 4% (at $r_d/r_t = 0.2$), the maximum degree of oblateness increases from 1.003 to 1.008, while a further reduction to 1% (at $r_d/r_t = 0.1$) increases the maximum α only slightly, to 1.009. Similar convergence of the Re at which transition to prolateness occurs is suggested by the small change from $Re_{\alpha=1} = 145$ to $Re_{\alpha=1} = 155$ between $r_d/r_t = 0.2$ and 0.1. These results are consistent with the transient prolate drop shape computed by Haywood, Renksizbulut, and Raithby (1994a) in an unbounded domain, and suggest that the effects of nonzero r_d/r_t are indeed small for $r_d/r_t = 0.1$.

The fact that the dependence of axis ratio on r_d/r_t is stronger as Re increases, clearly distinguishes the effect from conventional blockage in air and water tunnels, where wall effects tend to become progressively less important as Re increases. The difference would seem to be due to the fact that the computed drop motion in a tube gives rise to no mean flow, in contradistinction to the fan- or pump-driven shear flow situation in a wind or water tunnel.

2.3.2. Model Fluid Pair of Dandy and Leal

Figure 24a shows contours of constant axis ratio in the $Re-We$ and $Re-Ca$ planes, respectively, for density ratio $\rho_d/\rho_c = 100$ and viscosity ratio $\mu_d/\mu_c = 1000$. This combination of property value ratios, previously considered by Dandy and Leal (1989), was selected for its similarity to the water/air case, and also because drag coefficients for two $Re-We$ combinations at this combination of property value ratios were previously reported by Dandy and Leal. For the two cases reported by Dandy and Leal ($Re = 60$ and $We = 4$, and $Re = 20$ and

$We = 1$), drag coefficients computed using our code (1.63 and 2.69) compare well to values reported by Dandy and Leal (1.66 and 2.71). (A discussion of the likely causes of small discrepancies between our results and those of Dandy and Leal can be found in Bozzi et al. (1997).) Computations beyond the highest values of Re shown on each curve suffered from problematic convergence, and are not shown.

For $0 < We \leq 12$ and $0 < Re < 4000$, Figure 24a also shows that qualitatively different contours are found than for water drops in air (Figure 16). Although the $\alpha = 1$ contour intersects the $We = 0$ axis, Re does not remain constant on this contour over the entire range of We considered, but rather increases superlinearly with We .

For oblate drops ($\alpha > 1$), Re on the contours increases with increasing We as was the case on the $\alpha = 1$ contour. There is no indication of the vertical or horizontal asymptotes seen in the water/air case.

For prolate drops ($\alpha < 1$), the contours strongly suggest a vertical asymptote at $We = 0$. As opposed to the water/air case, the prolate-drop contours do not appear to have horizontal asymptotes. The Reynolds number initially decreases with increasing We , and then increases.

Figure 24b shows the corresponding constant axis ratio contours in the $Re-Ca$ plane. We again note the significant qualitative difference between this and the water/air case of Figure 17. For the unit axis ratio contour, there is a limit point on the $Ca = 0$ axis, and a turning point near $Ca = 0.006$, beyond which Re increases rapidly with decreasing Ca , suggesting a vertical asymptote on the $Ca = 0$ axis.

For prolate drops ($\alpha = 0.9$ and 0.95), a vertical asymptote at $Ca = 0$ is clearly apparent. The turning point observed on the $\alpha = 1$ contour is also seen for the prolate drop contours. For $\alpha = 0.95$ and 0.9 , the turning points are near $Ca = 0.005$ and 0.004 , respectively. As for the $\alpha = 1$ contour, an asymptote at $Ca = 0$ is evident.

For the oblate drop contour shown ($\alpha = 1.2$), a horizontal asymptote at $Re = 0$ is apparent. At lower Ca values, the results suggest a possible vertical asymptote, but that is unclear.

2.4. Discussion

In this section, we discuss previous reports of oblate drop shapes for liquid drops, and discuss why prolate drops have not been previously observed or predicted.

Pioneering experimental work by Pruppacher and Beard (1969) clearly demonstrated that water drops suspended by an upward flow in a vertical wind tunnel are oblate. That result is supported by approximate analytical work of Beard, Feng, and Chuang (1989), which considered steady axisymmetric motion of charged and uncharged raindrops falling through still air, and used the pressure distributions for steady axisymmetric flow past fixed spheres computed by LeClair, Hamielec, and Pruppacher (1970) and measured by Fage (1937) to estimate deformation of a liquid drop at the same Re . The drop shapes predicted were all oblate. That is to be expected, since the approximate analysis neglects the fact that water drops of the size considered support considerable internal circulation, and have mobile interfaces on which the velocity tangential to the interface does not vanish. As a result, the pressure distributions used by Chuang et al. and those that correspond to a drop with a mobile interface will be quite different. It is, therefore, not surprising that the axis ratios predicted by the approximate theory, using rigid-sphere pressure distributions, differ from those we have computed from the Navier-Stokes equations with full account being taken of flow in the drop and on its surface, and the normal force balance.

On the other hand, our computations show that water drops falling through air should be slightly prolate for Reynolds numbers between about 150 and 260, corresponding to drop diameters between 750 and 1000 microns. Beyond 1000 microns, rain drops are known to oscillate (Pruppacher & Klett, 1997).

Consistent with the hypothesis of Haywood, Renksizbulut, and Raithby (1994a), we suggest that the oblateness of the drops observed in the experiments of Pruppacher and Beard is an artifact of accumulation of flow visualization particles (average size reported by the authors as 5 μm) deliberately introduced into the drops, and organic species present in the late-1960's ambient atmosphere of Los Angeles. Surface-active species at the liquid/air interface will tend

to accumulate at the rear of the drop, with the effect becoming increasingly important as Re increases (Sadhal & Johnson 1983). Sadhal and Johnson (1983) have also shown that such nonuniform accumulation greatly reduces interfacial mobility everywhere on the drop surface, with the result that the drop tends to behave much like a rigid sphere. Reduced interfacial mobility and surface velocity give rise to a surface pressure distribution very similar to that for a rigid sphere, as used by Chuang et al. (1989). On the other hand, a more mobile interface, with zero velocity at the forward and rear stagnation points and maximum velocity near the equator, will give rise to a liquid-side pressure distribution with maxima at the stagnation points and a minimum near the equator. The effect, through the normal stress balance, is to increase interfacial curvature at the front and rear, and reduce curvature near the equator, as discussed by Foote (1969). The result is a more prolate (or less oblate) drop. An argument in support of this hypothesis follows.

First, note that the carbon particles added to the drop by Pruppacher and Beard were used to visualize and measure the tangential velocity (relative to the center-of-mass velocity) at the equator of one drop, with $r_d = 355 \mu\text{m}$ ($2r_d = 710 \mu\text{m}$). The measured equatorial velocity of $(2.7 \pm 0.8) \text{ cm sec}^{-1}$ is much smaller than our computed equatorial value of $\sim 13 \text{ cm sec}^{-1}$ or our computed maximum tangential velocity of $\sim 14.5 \text{ cm sec}^{-1}$, both for the same drop size.

Table 6 strongly suggests that "blockage" at $r_d/r_t = 0.1$ contributes very little to the discrepancy between the computed and measured equatorial velocities. The computed equatorial velocities at $r_d/r_t = 0.1$ and 0.2 differ by less than 0.8% and the maximum tangential velocities by less than 1%, with the smaller value of r_d/r_t giving rise to the slightly larger tangential velocity in each case, as would be expected on simple physical grounds. The computed Reynolds number (132.04) at $r_d/r_t = 0.1$ is very close to the value reported by Pruppacher and Beard ($Re = 135$). It is clear from the tabulated values that while significant error would occur if the unbounded flow was computed on a domain with $r_d/r_t = 0.5$, the residual error associated with wall effects at $r_d/r_t = 0.1$ is quite small.

Further support for the importance of accumulated surface-active species in the vertical wind tunnel experiments of Pruppacher and Beard (1970) comes from several sources. Gill et al. (1983) have shown that surface-active species found in collected rainwater significantly reduce surface tension and probably lead to formation of surface films. Kawamura and Kaplan (1984) and Kawamura, Steinberg, and Kaplan (1996) have reported collected rainwater concentrations of surface-active monocarboxylic and dicarboxylic acids that, by themselves (i.e., exclusive of aliphatic and aromatic hydrocarbons, aldehydes, ketones, organic nitrites, and other atmospheric organics, etc.) are of the order estimated by Gill et al. (1983) to be required to form a monolayer film. We note that most of the measurements of Kaplan and co-workers were made only several hundred yards from the air intake of the vertical wind tunnel of Pruppacher and Beard, and at a time (1982-1983) after air quality in Los Angeles had improved significantly (Cahill, Morales & Miranda 1996; Lonneman, 1998), with the concentration of volatile oxygen compounds in the Los Angeles Basin having decreased by a factor of three between 1968 and 1997 (Lonneman, 1998).

Finally, measurements for collected rainwater actually understate the situation, because the first-falling rain is the most contaminated (cf. Kawamura and Kaplan (1986) and Kawamura, Steinberg and Kaplan 1996), and subsequent drops fall through an air column from which organic species have largely been scavenged. Thus, any time-integrated (e.g., "collected") rainwater sample underestimates the gas-phase concentration of scavengeable species. In the experiments of Pruppacher and Beard, the drops were suspended at constant elevation in the air flow with residence time on the order of minutes (LeClair, Hamielec, Pruppacher & Hall, 1972), with "fresh" contaminated air continuously supplied to the drop by the open-return type UCLA vertical wind tunnel (Pruppacher & Neiburger, 1968; Beard, private communication, 2001). The effect is identical to a raindrop falling through an air column that is never depleted of scavengeable species.

3. Trajectories of Water Drops Injected into Air

3.1. Background

A critical issue in the design of spray systems is the nature of the trajectories followed by drops of various sizes as a function of their initial position (the injection point) and initial velocity (magnitude and direction). If the flow is turbulent, then identical drops with identical injection positions and velocities will follow different trajectories. In steady flows, all drops of a given size and with specified injection condition will follow the same trajectory.

The nature of the trajectory is frequently important in determining whether all drops have "thermal histories" sufficient to effect complete evaporation or combustion. Since this typically depends on the velocity history of the drop as it passes through (or around) a flame zone, the importance of the trajectory is clear. Sufficiently small drops tend to follow the instantaneous streamlines of the flow better than their larger counterparts, so in a well-designed system, the drops of interest are at the large end of the size spectrum, with which most emissions are associated. For these large drops, one would expect that interface deformation can play a significant role, depending on drop size and speed.

Trajectories of liquid drops in production-scale reactors can be significantly influenced by the turbulent nature of the flow field, with the importance of turbulent fluctuations being more pronounced for larger drops due to the greater importance of inertial effects. Prediction of drop trajectories in turbulent flows requires detailed understanding of both the flow field and drop dynamics, including the instantaneous orientation of the drop as well as its response to velocity fluctuations with length scales comparable to the characteristic drop size.

A more tractable problem is that of computing drop trajectories in an otherwise steady laminar flow such as that which obtains in laboratory-scale combustors (e.g., Davis, Gale, and Wendt, 2000; Davis, Gale, Wendt, and Linak, 1998). Absent swirl, the flow in such a combustor is, to an excellent degree of approximation, steady, axisymmetric, and purely axial. Thus, if a drop is injected collinearly with the flow, and if the drop is not so large that its trajectory is

significantly affected by gravity (Mulholland et al., 1991) then the drop trajectory will be purely axial. In that event, the drop trajectory can be determined by solving a single ordinary differential equation for the center-of-mass velocity of the drop. That is the approach taken in what follows.

3.2. Trajectory Formulation

The equation of motion $F = ma$ for a drop is given by:

$$\rho_d \pi \frac{4}{3} r_d^3 \frac{dU_{axis}}{dt} = -C_D \frac{1}{2} \rho_c U_{axis}^2 \pi r_d^2 \quad (27)$$

where ρ_d , ρ_c , r_d , C_D , and U_{axis} are the density of the drop, density of the continuous phase, radius of the drop, coefficient of drag, and center-of-mass velocity of the drop relative to the gas, respectively.

Rearranging (27), we obtain the ordinary differential equation

$$\frac{dU_{axis}}{dt} = -\frac{3}{8} \frac{\rho_c}{\rho_d r_d} C_D U_{axis}^2 \quad (28)$$

where $U_{axis} = U_{axis}(t; r_d)$, C_D depends on U_{axis} through $Re = 2\rho_c r_d U_{axis} / \mu_c$, and

$$U_{axis}(0; r_d) = U_o. \quad (29)$$

The drag coefficients are computed by the Navier-Stokes code described in §2.2.2. Using this code, a series of C_D values for each drop size is computed for initial drop velocities U_o ranging from 0.007 msec^{-1} to 10 msec^{-1} . These C_D values (shown in Tables 7 and 8) are then corrected for wall effects using an equation

$$C_D = C_{D\infty} + (24/Re)(K - 1) \quad (30)$$

proposed by Fayon and Happel (Clift, Grace and Weber, 1978), where K is given by Haberman and Sayre (1958) as

$$K = \frac{1 - 0.75857\lambda^5}{1 - 2.1050\lambda + 2.0865\lambda^3 - 1.7068\lambda^5 + 0.72603\lambda^6} \quad (31)$$

and $\lambda = r_d/r_i$ is the radius ratio. The "wall-corrected" values are shown in Tables 9 and 10.

For each drop size, the functional form

$$C_D = A + \frac{B}{Re^{1/2}} + \frac{C}{Re} \quad (32)$$

is then fitted to the corrected C_D values by linear least-squares, yielding the coefficients in Table 11. The mean squared relative error increases monotonically from 0.1% at $2r_d = 100 \mu\text{m}$ to about 0.5% at $2r_d = 1200 \mu\text{m}$.

The temporal variation of the center-of-mass velocity of each drop is then obtained by numerically integrating (28) using the modified Euler's method. With U_{axis} known at $t = t_o$, the value $U_{axis,pre}(t_{n+1})$ is estimated or "predicted" at time t_{n+1} using Euler's method

$$U_{axis,pre}(t_{n+1}) = U(t_n) + \Delta t f(t_n), \quad (33)$$

where

$$f(t) = -\frac{3}{8} \frac{\rho_c}{\rho_d r_d} C_D U_{axis}^2 \quad (34)$$

is the right-hand side of (28). We can then use (33) to compute $f_{pre}(t_{n+1})$, giving an improved or "corrected" estimate

$$U_{axis,corr}(t_{n+1}) = U(t_n) + \Delta t \frac{f(t_n) + f_{pre}(t_{n+1})}{2}. \quad (35)$$

The time step, Δt , is estimated using the analytical solution of the first-order ordinary differential equation

$$\frac{dx}{dt} = -ax^2 \quad (36)$$

subject to the initial condition $x(0) = x_o$. This is a model of (28), being equivalent if C_D is independent of U_{axis} . The solution of (36) is

$$x(t) = \frac{x_o}{1 + ax_o t}, \quad (37)$$

from which we find the initial (i.e., $t = 0$) characteristic time to be

$$\frac{x_o}{dx/dt|_0} = -\frac{1}{ax_o}. \quad (38)$$

We then choose

$$\Delta t = \frac{0.04}{ax_o} = \frac{0.04}{U_{axis}(0; r_d)} \frac{8}{3} \frac{\rho_d r_d}{\rho_c C_D}. \quad (39)$$

Integration is terminated when the condition

$$\frac{U_{axis}(t; r_d)}{U_{axis}(0; r_d)} \leq 10^{-3} \quad (40)$$

is satisfied, corresponding to near-coincidence of the drop trajectory with a pathline in the external flow.

To validate the adequacy of the time-step size used, we performed the integration with half the time-step, $\Delta t = 0.02/(ax_o)$, and found the maximum relative difference to be less than 0.01%, thus confirming the adequacy of the time-step size (39) used.

3.3. Results

We present dimensional and dimensionless variations of U_{axis} and U_{axis}/U_o for each of the four drop sizes ($\chi = 8.79 \times 10^3$, 3.52×10^4 , 6.15×10^4 , and 1.05×10^5 , corresponding to $2r_d = 100$, 400, 700, and 1200 μm , respectively) discussed in Chapter 2. The initial relative velocities U_o range from 0.007 to 10 m sec^{-1} .

For the smallest drop ($\chi = 8.79 \times 10^3$, corresponding to $2r_d = 100 \mu\text{m}$), Figure 25a shows the temporal variation of the dimensional relative velocity. When the initial relative velocity U_o (and hence Re) is small, the drag coefficient is nearly proportional to Re (and hence U_{axis}), so that the right-hand side of (28) is almost exactly proportional to U_{axis} . Hence, at low values of U_{axis} , the solution of (28) decays nearly exponentially in time. At higher U_o , the dependence of C_D on Re is less well approximated by an inverse relationship, and departures from linearity are more severe, resulting in significantly nonexponential decay of the relative

velocity. As the relative velocity decreases, departures from linearity become insignificant, and the drop velocity exponentially approaches the free-stream velocity.

In Figure 25b, we show the dimensionless temporal variation of the velocity ratio (U_{axis}/U_o), where the dimensionless time is defined as tv/r_d^2 . At small relative velocities, the velocity adjustment is again essentially exponential. As U_o increases, we again see an initially rapid decrease in the relative velocity, followed by an ultimately exponential approach to the free-stream value as the relative drop velocity decreases.

For the medium-size drop ($\chi = 3.52 \times 10^4$ corresponding to $2r_d = 400 \mu\text{m}$) Figures 26(a,b) show the temporal variation of the dimensional relative velocity and dimensionless time velocity ratio, respectively. The results are qualitatively similar to those for the smaller drop. At low values of U_o , the exponential decay of relative velocity is again apparent. At higher values of U_o departure from linearity are more pronounced than for the smaller drop and are evident at a lower injection speeds. We also note that for drops with a given injection velocity, the time required for the relative velocity to fall to a given level is nearly 20 times higher than for the smaller drop. Comparison of Figures 25b and 26b shows that the *dimensionless* time required for the relative velocity to decay to some specified level is relatively independent of drop size, with the initially-slowest drop taking more time for the larger case and the initially-fastest drop requiring less time at $2r_d = 400 \mu\text{m}$ than at $100 \mu\text{m}$.

For the next largest drop ($\chi = 6.15 \times 10^4$, corresponding to $2r_d = 700 \mu\text{m}$), Figure 27a shows an even more nonexponential initial decay of relative drop velocity. The time required for a drop with a given initial speed to fall to a specified relative velocity is increased by another factor of three. Comparison of Figure 27b to Figure 26b shows that the dependence of relative velocity on drop size and injection velocity is similar to the differences between the 100 and $400 \mu\text{m}$ drops.

Figures 28(a,b) show that these trends continue for the largest drop considered ($\chi = 1.05 \times 10^5$ corresponding to $2r_d = 1200 \mu\text{m}$).

4. Conclusion

We have presented the first computational results for steady axisymmetric motion of liquid drops through a gas at intermediate Reynolds numbers (as high as 775). A remarkable result of this work is the prediction that water drops falling through air are oblate below a certain size and become prolate as the drop size increases. Careful consideration of the details of previous experiments and the mechanism by which adsorbed surface-active species affect interfacial mobility of liquid drops, allows this result to be reconciled with previous experimental work that had revealed only oblate drops, and with approximate analytical work that had predicted only oblate drops.

The decay of the relative velocity of a deformable drop injected collinearly with a uniaxial flow is shown to be nearly exponential when the injection velocity is sufficiently small. As the injection velocity increases, the decay of the drop velocity to the free-stream value becomes progressively nonexponential. As the drop size increases, the range of velocities for which nonexponential decay occurs increases.

References

- Beard, K.V. 1976 Terminal fall velocity and shape of cloud and precipitation drops aloft. *J. Atmos. Sci.* **33**, 851-864.
- Beard, K.V., Feng, J.Q., & Chuang, C. 1989 A simple perturbation model for the electrostatic shape of falling drops. *J. Atmos. Sci.* **46**, 2404-2418.
- Bozzi, L. 1995 *Steady axisymmetric motion of deformable drops falling or rising through a homoviscous fluids in a tube at intermediate Reynolds numbers*. MS Thesis, University of Illinois.
- Bozzi, L., Feng, J.Q., Scott, T.C., & Pearlstein, A.J. 1997 Steady axisymmetric motion of deformable drops falling or rising through a homoviscous fluid in a tube at intermediate Reynolds number. *J. Fluid Mech.* **336**, 1-32.
- Bozzi, L.A., Mantle, W.J., Pearlstein, A.J., & Feng, J.Q. 1996 Density ratio effects on steady, axisymmetric motion of deformable drops falling or rising through a homoviscous fluids in a tube at intermediate Reynolds numbers. *Bull. Am. Phys. Soc.* **41**, 1767.
- Cahill, T.A., Morales, R. & Miranda, J. 1996 Comparative aerosol studies of Pacific Rim cities – Santiago, Chile (1987); Mexico City, Mexico (1987-1990); and Los Angeles, U.S.A. (1973-1987). *Atmos. Environ.* **30**, 747-749
- Capel, P.D., Leuenberger, C. & Giger, W. 1991 Hydrophobic organic chemicals in urban fog. *Atmos. Environ.* **25A**, 1335-1346.
- Christodoulou, K.N. & Scriven, L.E. 1989 The fluid mechanics of slide coating. *J. Fluid Mech.* **208**, 321-354.
- Christodoulou, K.N. 1990 *Computational Physics of Slide Coating Flow*. Ph.D. Thesis, University of Minnesota.
- Christodoulou, K.N. & Scriven, L.E. 1992 Discretization of free surface flows and other moving boundary problems. *J. Comp. Phys.* **99**, 39-55.
- Clift, R., Grace, J.R. & Weber, M.E. 1978 *Bubbles, Drops, and Particles*. Academic Press, New York.
- Coutanceau, M. & Thizon, P. 1981 Wall effect on the bubble behavior in highly viscous liquids. *J. Fluid Mech.* **107**, 339-373.
- Dandy, D.S. & Leal, L.G. 1989 Buoyancy-driven motion of a deformable drop through a quiescent liquid at intermediate Reynolds numbers. *J. Fluid Mech.* **208**, 161-192.
- Davis, S.B., Gale, T.K. & Wendt, J.O.L. 2000 Competition for sodium and toxic metals capture on sorbents. *Aerosol Sci. Technol.* **32**, 142-151
- Davis, S.B., Gale, T.K., Wendt, J.O.L. & Linak, W.P. 2000 Multicomponent coagulation and condensation of toxic metals in combustors. *Proceedings of the 27th (International) Symposium on Combustion*, **2**, 1785-1791, The Combustion Institute, Pittsburgh, Penn.
- de Santos, J.M. 1991 *Two-Phase Cocurrent Downflow through Constricted Passages*, Ph.D. Thesis, University of Minnesota.
- Eiseman, P.R. 1982a Coordinate generation with precise controls over mesh properties. *J. Comput. Phys.* **47**, 331-351.
- Eiseman, P.R. 1982b High level continuity for coordinate generation with precise controls. *J. Comput. Phys.* **47**, 352-374.

- Fage, A. 1937 Experiments on a sphere at critical Reynolds numbers. Aero. Res. Comm., (Great Britain), Rep. and Memo. No. 1766.
- Foote, G.B. 1969 On the internal circulation and shape of large raindrops. *J. Atmos. Sci.* 26, 179-181.
- Gill, P.S., Graedel, T.E. & Weschler, C.J. 1983 Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snowflakes. *Rev. Geophys. Space Phys.* 21, 903-920.
- Haberman, W.L. & Sayre, R.M. 1958 *Motion of Rigid and Fluid Spheres in Stationary and Moving Liquids inside Cylindrical Tubes*, David Taylor Model Basin Report 1143.
- Haywood, R.J., Renksizbulut, M. & Raithby, G.D. 1994a Transient deformation and evaporation of droplets at intermediate Reynolds numbers. *Int. J. Heat Mass Transfer*, 37, 1401-1409.
- Haywood, R.J., Renksizbulut, M. & Raithby, G.D. 1994b Numerical solution of deforming evaporating droplets at intermediate Reynolds numbers. *Numer. Heat Transfer, A* 26, 253-272.
- Hood, P. 1976 Frontal solution program for unsymmetrical matrices. *Int. J. Num. Meth. Eng.* 10, 379-399. [See *ibid.* 11, 1055 (1977) for corrigendum.]
- Huyakorn, P.S., Taylor, C., Lee, R.L. & Gresho, P.M. 1978 A comparison of various mixed interpolation finite elements in the velocity-pressure formulation of the Navier-Stokes equations. *Computers and Fluids*, 6, 25-35.
- Johnson, T.A., & Patel, V.C. 1999 Flow past a sphere up to a Reynolds number of 300 *J. Fluid Mech.* 378, 19-70
- Kawamura, K. & Kaplan, I.R. 1984 Capillary gas chromatography determination of volatile organic acids in rain and fog samples. *Anal. Chem.* 9, 7-26.
- Kawamura, K. & Kaplan, I.R. 1986 Compositional changes of organic matter in rainwater during precipitation events. *Atmos. Environ.* 20, 527-535.
- Kawamura, K., Steinberg, S. & Kaplan, I.R. 1996 Concentrations of monocarboxylic and dicarboxylic acids and aldehydes in southern California wet precipitations: Comparison of urban and nonurban samples and compositional changes during scavenging. *Atmos. Environ.* 30, 1035-1052.
- Keller, H.B. 1977 Numerical solution of bifurcation and nonlinear eigenvalue problems, in *Applications of Bifurcation Theory* (ed. P. Rabinowitz), pp. 359-384, Academic Press, New York.
- Kim, I. 1989 Numerical study of the onset of instability in the flow past a sphere. Ph.D. Thesis, University of Arizona.
- Kistler, S.F. & Scriven, L.E. 1983 Coating Flows, in *Computational Analysis of Polymer Processing* (eds. J.R.A. Pearson and S.M. Richardson), pp. 243-299, Applied Science Publishers, New York.
- Lamb, H. 1932 *Hydrodynamics*, 6th edition. Cambridge University Press, Cambridge.
- Le Clair, B.P., Hamielec, A.E. & Pruppacher, H.R. 1970 A numerical study of the drag on a sphere at low and intermediate Reynolds number. *J. Atmos. Sci.* 27, 308-315.
- Le Clair, B.P., Hamielec, A.E., Pruppacher, H.R. & Hall, W.D. 1972 A theoretical and experimental study of the internal circulation in water drops falling at terminal velocity in air. *J. Atmos. Sci.* 29, 728-740

- Lonneman, W.A. 1998 Comparison of hydrocarbon composition in Los Angeles for the year 1968 and 1997. *Proceedings of the Specialist Conference on Measurement of Toxic and Related Air Pollutants*, 1, 356-365, Air and Waste Management Association, Pittsburgh, Penn.
- Mantle, W.J. 2000 Use of improved far-field boundary conditions to compute external flows on reduced domains. Ph.D. Thesis, University of Illinois.
- Mulholland, J.A., Srivastava, R.K., Wendt, J.O.L., Agrawal, S.R. & Lanier, W.S. 1991 Trajectory and incineration of rogue droplets in a turbulent diffusion flame. *Combustion and Flame*, 86, 297-310.
- Perona, M.J. 1992 The solubility of hydrophobic compounds in aqueous droplets. *Atmos. Environ.* 26A, 2549-2555.
- Pruppacher, H.R. & Beard, K.V. 1970 A wind tunnel investigation of the internal circulation and shape of water drops falling at terminal velocity in air. *Quart. J. Roy. Met. Soc.* 96, 247-256.
- Pruppacher, H.R. & Klett, J.D. 1978 *Microphysics of Clouds and Precipitation*. D. Reidel, Dordrecht.
- Pruppacher, H.R. & Neiburger, M. 1968 The UCLA Cloud Tunnel. *Proc. Fifth Int. Conf. on Cloud Physics* Toronto, pp. 389-392.
- Pruppacher, H.R. & Pitter, R.L. 1971 A semi-empirical determination of the shape of cloud and rain drops. *J. Atmos. Sci.* 28, 83-94.
- Riks, E. 1972 The application of Newton's method to the problem of elastic stability. *J. Appl. Mech.* 39, 1060-1065.
- Sadhal, S.S. & Johnson, R.E. 1983 Stokes flow past bubbles and drops partially coated with thin films. Part 1. Stagnant cap of surfactant film – exact solution. *J. Fluid Mech.* 126, 237-250.
- Strang, G. & Fix, G.J. 1973 *An Analysis of the Finite Element Method*. Prentice-Hall, Englewood Cliffs, N.J.
- Thompson, J.F., Warsi, Z.U.A. & Mastin, C.W. 1982 Boundary-fitted coordinated systems for numerical solution of partial differentialequations – a review. *J. Comput. Phys.* 47, 1-108.
- Thompson, J.F., Warsi, Z.U.A. & Mastin, C.W. 1985 *Numerical Grid Generation*. Elsevier, New York.
- Walters, R.A. 1980 The frontal method in hydrodynamics simulations. *Computers and Fluids* 8, 265-272.
- Wendt, J.O.L. 1994 Combustion science for incinerator technology. *Twenty-fifth Symposium (International) on Combiustion*, 277-289, The Combustion Institute, Pittsburgh, Penn.
- Winnikow, S. 1965 *Motion and Heat Transfer of Droplets at Large Reynolds and Peclet Number*, Ph.D. Thesis, University of Illinois at Urbana-Champaign.
- Winnikow, S. & Chao, B.T. 1966 Droplet motion in purified systems. *Phys. Fluids*, 9, 50-61.

Tables

U (msec ⁻¹)	Re	$C_{D, comp}$	$C_{D, std}$	α_{comp}
0.007	0.0452	526.03	535.45	1.0000
0.015	0.0969	245.54	252.02	1.0000
0.035	0.2260	105.36	110.12	1.0000
0.07	0.4520	52.909	56.684	1.0000
0.15	0.9687	25.164	27.951	1.0000
0.3	1.9373	13.286	15.164	1.0000
0.6	3.8747	7.4639	8.5707	1.0001
1.6	10.332	3.6887	4.1642	1.0005
2.5	16.144	2.7753	3.1036	1.0010
4	25.831	2.0985	2.3258	1.0021
5	32.289	1.8495	2.0295	1.0030
6.5	41.976	1.6021	1.7391	1.0044
7.5	48.433	1.4844	1.6027	1.0053
8.5	54.891	1.3903	1.4944	1.0062
10	64.578	1.2786	1.3672	1.0074
12.5	80.722	1.1424	1.2141	1.0089
15	96.866	1.0435	1.1048	1.0093
17.5	113.01	0.9668	1.0220	1.0085
20	129.16	0.9046	0.9564	1.0059
22.5	145.30	0.8521	0.9030	1.0016
25	161.44	0.8066	0.8583	0.9954
27.5	177.59	0.7660	0.8202	0.9872

Table 1. Re , computed drag coefficients, "standard" rigid-sphere drag coefficients and axis ratios for water drops in air for $\chi = 8.79 \times 10^3$ and $2r_d = 100 \mu\text{m}$ as a function of drop speed.

U (msec ⁻¹)	Re	$C_{D, comp}$	$C_{D, std}$	α_{comp}
0.007	0.1808	131.63	136.76	1.0000
0.015	0.3874	61.634	65.611	1.0000
0.035	0.9041	26.883	29.759	1.0000
0.07	1.8082	14.123	16.088	1.0000
0.15	3.8747	7.4638	8.5707	1.0000
0.3	7.7493	4.4807	5.0902	1.0001
0.6	15.499	2.8456	3.1855	1.0003
1.6	41.330	1.6134	1.7547	1.0011
2.5	64.578	1.2754	1.3672	1.0018
4	103.32	1.0074	1.0691	1.0023
5	129.15	0.9137	0.9564	1.0015
6.5	167.90	0.7982	0.8424	0.9979
7.5	193.73	0.7406	0.7873	0.9935
8.5	219.56	0.6926	0.7427	0.9872
10	258.31	0.6324	0.6894	0.9745

Table 2. Re , computed drag coefficients, "standard" rigid-sphere drag coefficients and axis ratios for water drops in air for $\chi = 3.52 \times 10^4$ and $2r_d = 400 \mu\text{m}$ as a function of drop speed.

U (msec ⁻¹)	Re	$C_{D, comp}$	$C_{D, std}$	α_{comp}
0.007	0.3164	75.362	79.618	1.0000
0.015	0.6781	35.519	38.766	1.0000
0.035	1.5822	15.923	18.06	1.0000
0.07	3.1643	8.7707	10.08	1.0000
0.15	6.7807	4.9201	5.6047	1.0000
0.3	13.561	3.0937	3.4728	1.0001
0.6	27.123	2.0392	2.2566	1.0003
1.6	72.327	1.2032	1.2866	1.0012
2.5	113.01	0.9786	1.0220	1.0012
4	180.82	0.7663	0.8133	0.9976
5	226.02	0.6845	0.7328	0.9914
6.5	293.83	0.5925	0.6575	0.9753
7.5	339.03	0.5443	0.6258	0.9598
8.5	384.24	0.5027	0.6007	0.9408
10	452.04	0.4497	0.5714	0.9070

Table 3. Re , computed drag coefficients, "standard" rigid-sphere drag coefficients and axis ratios for water drops in air for $\chi = 6.15 \times 10^4$ and $2r_d = 700 \mu\text{m}$ as a function of drop speed.

U (msec ⁻¹)	Re	$C_{D, comp}$	$C_{D, std}$	α_{comp}
0.007	0.5425	44.200	47.739	1.0000
0.015	1.1624	21.171	23.717	1.0000
0.035	2.7123	9.9560	11.429	1.0000
0.07	5.4245	5.7810	6.6120	1.0000
0.15	11.6240	3.4147	3.8455	1.0000
0.3	23.2468	2.2292	2.4845	1.0002
0.6	46.496	1.5140	1.6402	1.0004
1.6	123.99	0.9327	0.9759	1.0006
2.5	193.77	0.7428	0.7872	0.9978
4	309.97	0.5827	0.6453	0.9819
5	387.47	0.5079	0.5991	0.9622
6.5	503.71	0.4276	0.5538	0.9198
7.5	581.20	0.3849	0.5326	0.8849
8.5	658.69	0.3484	0.5159	0.8466
10	774.93	0.3028	0.4966	0.7869

Table 4. Re , computed drag coefficients, "standard" rigid-sphere drag coefficients and axis ratios for water drops in air for $\chi = 1.05 \times 10^5$ and $2r_d = 1200 \mu\text{m}$ as a function of drop speed.

$2r_d$	Re	α	z_{s2}	$r_d z_{s2}$
50	0.1902	1.0000	0	0
100	1.4629	1.0000	0	0
200	8.6723	1.0002	0	0
300	21.796	1.0006	0	0
400	40.522	1.0011	0.5297	106
500	64.611	1.0015	1.0689	267
600	93.898	1.0016	1.5694	471
800	167.93	0.9989	2.4406	976
900	213.00	0.9950	2.7950	1258
1000	263.99	0.9881	3.0816	1541
1200	386.65	0.9624	3.4497	2070
1400	544.17	0.9135	3.5591	2491
1500	640.07	0.8780	3.5349	2651

Table 5. Reynolds number, axis ratio, dimensionless and dimensional recirculation zone length for falling water drops in air as a function of drop diameters.

r_d/r_t	Re	U (cmsec ⁻¹)	$U_{\theta,eq}$ (cmsec ⁻¹)	$U_{\theta,max}$ (cmsec ⁻¹)
0.1	132.04	287.98	12.96	14.31
0.2	127.78	278.70	12.87	14.18
0.5	79.87	174.21	6.56	6.86

Table 6. Re , drop velocity, equatorial velocity, and maximum tangential velocity for $2r_d = 710 \mu\text{m}$ at $r_d/r_t = 0.1, 0.2$ and 0.5 .

$2r_d$ (μm)		Drop Velocity (m sec^{-1})														
		0.007	0.015	0.035	0.07	0.15	0.3	0.6	1.6	2.5	4	5	6.5	7.5	8.5	10
100	Re	0.0452	0.0969	0.2260	0.4520	0.9687	1.9373	3.8747	10.332	16.144	25.831	32.289	41.976	48.433	54.891	64.578
	C_D	665.83	310.77	133.32	66.889	31.688	16.547	9.0948	4.3003	3.1667	2.3431	2.0452	1.7526	1.6149	1.5054	1.3765
200	Re	0.0904	0.1937	0.4520	0.9041	1.9373	3.8747	7.7493	20.665	32.289	51.662	64.578	83.951	96.866	109.78	129.16
	C_D	332.96	155.49	66.889	33.872	16.547	9.0947	5.2962	2.6958	2.0442	1.5555	1.3743	1.1932	1.1064	1.0364	0.9525
300	Re	0.1356	0.2906	0.6781	1.3561	2.9060	5.8120	11.624	30.997	48.433	77.493	96.866	125.93	145.30	164.67	193.73
	C_D	222.03	103.77	44.838	22.997	11.577	6.5835	3.9585	2.0947	1.6127	1.2445	1.1057	0.9647	0.8960	0.8396	0.7705
400	Re	0.1808	0.3875	0.9041	1.8082	3.8747	7.7493	15.499	41.330	64.578	103.32	129.15	167.90	193.73	219.56	258.31
	C_D	166.58	77.943	33.872	17.617	9.0947	5.2962	3.2533	1.7663	1.3733	1.0686	0.9520	0.8316	0.7716	0.7216	0.6589
500	Re	0.2260	0.4843	1.1301	2.2602	4.8433	9.6867	19.373	51.662	80.722	129.16	161.44	209.88	242.17	274.46	322.89
	C_D	133.32	62.471	27.332	14.414	7.5945	4.5022	2.8097	1.5544	1.2169	0.9519	0.8489	0.7404	0.6853	0.6386	0.5793
600	Re	0.2712	0.5812	1.3561	2.7123	5.8120	11.624	23.248	61.995	96.866	154.99	193.73	251.85	290.60	329.35	387.47
	C_D	111.15	52.176	22.997	12.286	6.5834	3.9584	2.5011	1.4041	1.1049	0.8670	0.7728	0.6719	0.6197	0.5750	0.5179
700	Re	0.3164	0.6781	1.5822	3.1643	6.7807	13.561	27.123	72.327	113.01	180.82	226.02	293.83	339.03	384.24	452.04
	C_D	95.333	44.838	19.917	10.768	5.8521	3.5597	2.2722	1.2906	1.0196	0.8012	0.7132	0.6173	0.5671	0.5238	0.4685
800	Re	0.3616	0.7749	1.8082	3.6164	7.7493	15.499	30.997	82.659	129.16	206.65	258.31	335.80	387.47	439.13	516.62
	C_D	83.474	39.347	17.617	9.6277	5.2961	3.2532	2.0943	1.2013	0.9518	0.7480	0.6644	0.5721	0.5234	0.4813	0.4275
900	Re	0.4068	0.8718	2.0342	4.0684	8.7180	17.436	34.872	92.992	145.30	232.48	290.60	377.78	435.90	494.02	581.20
	C_D	74.257	35.087	15.835	8.7386	4.8577	3.0091	1.9515	1.1286	0.8961	0.7036	0.6233	0.5337	0.4862	0.4452	0.3930
1000	Re	0.4520	0.9687	2.2602	4.5204	9.6867	19.373	38.747	103.32	161.44	258.31	322.89	419.75	484.33	548.91	645.78
	C_D	66.889	31.688	14.413	8.0246	4.5022	2.8096	1.8337	1.0680	0.8493	0.6656	0.5879	0.5005	0.4541	0.4141	0.3634
1100	Re	0.4973	1.0655	2.4862	4.9725	10.655	21.311	42.621	113.66	177.59	284.14	355.18	461.73	532.77	603.80	710.35
	C_D	60.865	28.914	13.252	7.4376	4.2073	2.6428	1.7346	1.0164	0.8091	0.6325	0.5568	0.4714	0.4259	0.3869	0.3378
1200	Re	0.5425	1.1624	2.7123	5.4245	11.624	23.248	46.496	123.99	193.77	309.97	387.47	503.71	581.20	658.69	774.93
	C_D	55.850	26.608	12.286	6.9459	3.9583	2.5010	1.6499	0.9718	0.7739	0.6031	0.5292	0.4455	0.4010	0.3630	0.3155

Table 7. Computed Reynolds number and drag coefficients as a function of drop size and drop velocity, $U < 10 \text{ msec}^{-1}$.

$2r_d$ (μm)		Drop Velocity (m sec^{-1})						
		12.5	15	17.5	20	22.5	25	27.5
100	Re	80.722	96.866	113.01	129.16	145.30	161.44	177.59
	C_D	1.2207	1.1087	1.0227	0.9535	0.8956	0.8457	0.8016
200	Re	161.44	193.73	226.02	258.31	290.60		
	C_D	0.8476	0.7683	0.7038	0.6490	0.6011		

Table 8. Computed Reynolds number and drag coefficients as a function of drop size and drop velocity, $U > 10 \text{ msec}^{-1}$

$2r_d$ (μm)		Drop Velocity (m sec^{-1})														
		0.007	0.015	0.035	0.07	0.15	0.3	0.6	1.6	2.5	4	5	6.5	7.5	8.5	10
100	Re	0.0452	0.0969	0.2260	0.4520	0.9687	1.9373	3.8747	10.332	16.144	25.831	32.289	41.976	48.433	54.891	64.578
	C_D	526.03	245.54	105.36	52.909	25.164	13.286	7.4639	3.6887	2.7753	2.0985	1.8495	1.6021	1.4844	1.3903	1.2786
200	Re	0.0904	0.1937	0.4520	0.9041	1.9373	3.8747	7.7493	20.665	32.289	51.662	64.578	83.951	96.866	109.78	129.16
	C_D	263.07	122.87	52.909	26.883	13.286	7.4638	4.4807	2.3900	1.8485	1.4332	1.2764	1.1179	1.0412	0.9788	0.9142
300	Re	0.1356	0.2906	0.6781	1.3561	2.9060	5.8120	11.624	30.997	48.433	77.493	96.866	125.93	145.30	164.67	193.73
	C_D	175.43	82.024	35.519	18.337	9.4028	5.4962	3.4149	1.8908	1.4822	1.1630	1.0405	0.9145	0.8600	0.8059	0.7395
400	Re	0.1808	0.3875	0.9041	1.8082	3.8747	7.7493	15.499	41.330	64.578	103.32	129.15	167.90	193.73	219.56	258.31
	C_D	131.63	61.634	26.883	14.122	7.4638	4.4807	2.8456	1.6134	1.2754	1.0074	0.9137	0.7982	0.7406	0.6926	0.6324
500	Re	0.2260	0.4843	1.1301	2.2602	4.8433	9.6867	19.373	51.662	80.722	129.16	161.44	209.88	242.17	274.46	322.89
	C_D	105.36	49.424	21.740	11.618	6.2898	3.8498	2.4835	1.4321	1.1386	0.9030	0.8148	0.7106	0.6578	0.6129	0.5560
600	Re	0.2712	0.5812	1.3561	2.7123	5.8120	11.624	23.248	61.995	96.866	154.99	193.73	251.85	290.60	329.35	387.47
	C_D	87.856	41.303	18.337	9.9560	5.4961	3.4148	2.2293	1.3022	1.0397	0.8262	0.7417	0.6449	0.5948	0.5519	0.4971
700	Re	0.3164	0.6781	1.5822	3.1643	6.7807	13.561	27.123	72.327	113.01	180.82	226.02	293.83	339.03	384.24	452.04
	C_D	75.362	35.519	15.923	8.7707	4.9201	3.0937	2.0392	1.2032	0.9786	0.7663	0.6845	0.5925	0.5443	0.5027	0.4497
800	Re	0.3616	0.7749	1.8082	3.6164	7.7493	15.499	30.997	82.659	129.16	206.65	258.31	335.80	387.47	439.13	516.62
	C_D	66.000	31.193	14.122	7.8803	4.4806	2.8455	1.8904	1.1249	0.9135	0.7174	0.6377	0.5491	0.5024	0.4620	0.4103
900	Re	0.4068	0.8718	2.0342	4.0684	8.7180	17.436	34.872	92.992	145.30	232.48	290.60	377.78	435.90	494.02	581.20
	C_D	58.724	27.839	12.729	7.1853	4.1328	2.6467	1.7703	1.0606	0.8601	0.6764	0.5982	0.5123	0.4667	0.4273	0.3772
1000	Re	0.4520	0.9687	2.2602	4.5204	9.6867	19.373	38.747	103.32	161.44	258.31	322.89	419.75	484.33	548.91	645.78
	C_D	52.909	25.164	11.618	6.6267	3.8498	2.4834	1.6706	1.0251	0.8152	0.6411	0.5643	0.4804	0.4358	0.3975	0.3488
1100	Re	0.4973	1.0655	2.4862	4.9725	10.655	21.311	42.621	113.66	177.59	284.14	355.18	461.73	532.77	603.80	710.35
	C_D	48.157	22.983	10.711	6.1668	3.6142	2.3463	1.5863	0.9756	0.7766	0.6103	0.5344	0.4525	0.4088	0.3714	0.3242
1200	Re	0.5425	1.1624	2.7123	5.4245	11.624	23.248	46.496	123.99	193.77	309.97	387.47	503.71	581.20	658.69	774.93
	C_D	44.201	21.171	9.9560	5.7810	3.4147	2.2292	1.5140	0.9327	0.7428	0.5827	0.5079	0.4276	0.3849	0.3484	0.3028

Table 9. Computed Reynolds number and corrected drag coefficients as a function of drop size and drop velocity, $U < 10 \text{ m sec}^{-1}$.

$2r_d (\mu\text{m})$	Drop Velocity (m sec^{-1})							
	12.5	15	17.5	20	22.5	25	27.5	
100	80.722	96.866	113.01	129.16	145.30	161.44	177.59	
	1.1424	1.0435	0.9668	0.9046	0.8521	0.8066	0.7660	
200	161.44	193.73	226.02	258.31	290.60			
	0.8135	0.7374	0.6755	0.6229	0.5769			

Table 10. Computed Reynolds number and corrected drag coefficients as a function of drop size and drop velocity, $U > 10 \text{ msec}^{-1}$

$2r_d$ (μm)	A	B	C
100	0.6703	2.5151	22.2382
200	0.4570	3.6966	21.2352
300	0.3521	4.4458	20.4492
400	0.2799	5.0571	19.7296
500	0.2255	5.5541	19.0902
600	0.1826	5.9883	18.4900
700	0.1457	6.4156	17.8709
800	0.1163	6.7577	17.3371
900	0.0911	7.0705	16.8262
1000	0.0670	7.4141	16.2601
1100	0.0483	7.6700	15.8003
1200	0.0319	7.9061	15.3600

Table 11. Least-squares fit of $C_D = A + \frac{B}{Re^{1/2}} + \frac{C}{Re}$ for water drops of different sizes in air.

Figures

Figure 1. Definition Sketch

Figure 2a. Typical finite-element mesh of problem domain produced by elliptic mesh generator

Figure 2b. Detailed view of the finite-element mesh generated by the elliptic mesh generator in and near the drop.

Figure 3a. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 0.045$, corresponding to $2r_d = 100 \mu\text{m}$ at $U = 0.007 \text{ msec}^{-1}$.

Figure 3b. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 1.94$, corresponding to $2r_d = 100 \mu\text{m}$ at $U = 0.30 \text{ msec}^{-1}$.

Figure 3c. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 3.87$, corresponding to $2r_d = 100 \mu\text{m}$ at $U = 0.60 \text{ m sec}^{-1}$.

Figure 3d. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 25.83$, corresponding to $2r_d = 100 \mu\text{m}$ at $U = 4.0 \text{ msec}^{-1}$.

Figure 3e. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 41.98$, corresponding to $2r_d = 100 \mu\text{m}$ at $U = 6.5 \text{ msec}^{-1}$.

Figure 3f. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 64.58$, corresponding to $2r_d = 100 \mu\text{m}$ at $U = 10.0 \text{ msec}^{-1}$.

Figure 3g. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 96.87$, corresponding to $2r_d = 100 \mu\text{m}$ at $U = 15.0 \text{ msec}^{-1}$.

Figure 3h. Streamlines for $\chi = 8.79 \times 10^3$ and $Re = 177.59$, corresponding to $2r_d = 100 \mu\text{m}$ at $U = 27.5 \text{ msec}^{-1}$.

Figure 4. Axis ratio for $\chi = 8.79 \times 10^3$ and $0.045 \leq Re \leq 177.59$, corresponding to $2r_d = 100 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 27.5 \text{ msec}^{-1}$.

Figure 5. Position of the rear stagnation point, z_{s2} , for $\chi = 8.79 \times 10^3$ and $0.045 \leq Re \leq 177.59$, corresponding to $2r_d = 100 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 27.5 \text{ msec}^{-1}$.

Figure 6. Computed drag coefficient for $\chi = 8.79 \times 10^3$ and $0.045 \leq Re \leq 177.59$, corresponding to $2r_d = 100 \mu\text{m}$ with $0.007 \text{ m sec}^{-1} \leq U \leq 27.5 \text{ m sec}^{-1}$. Solid curve shows "standard" drag curve for rigid sphere.

Figure 7a. Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 0.18$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 0.007 \text{ m sec}^{-1}$.

Figure 7b. Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 3.87$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 0.15 \text{ msec}^{-1}$.

Figure 7c. Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 15.50$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 0.60 \text{ msec}^{-1}$.

Figure 7d. Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 41.33$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 1.6 \text{ msec}^{-1}$.

Figure 7e. Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 64.58$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 2.5 \text{ msec}^{-1}$.

Figure 7f. Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 129.15$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 5.0 \text{ msec}^{-1}$.

Figure 7g. Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 167.90$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 6.5 \text{ msec}^{-1}$.

Figure 7h. Streamlines for $\chi = 3.52 \times 10^4$ and $Re = 258.31$, corresponding to $2r_d = 400 \mu\text{m}$ at $U = 10.0 \text{ msec}^{-1}$.

Figure 8. Axis ratio for $\chi = 3.52 \times 10^4$ and $0.18 \leq Re \leq 258.31$, corresponding to $2r_d = 400 \mu\text{m}$ with $0.007 \text{ m sec}^{-1} \leq U \leq 10.0 \text{ m sec}^{-1}$.

Figure 9. Position of the rear stagnation point, z_{s2} , for $\chi = 3.52 \times 10^4$ and $0.18 \leq Re \leq 258.31$, corresponding to $2r_d = 400 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.

Figure 10a. Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 0.32$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 0.007 \text{ m sec}^{-1}$.

Figure 10b. Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 27.12$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 0.60 \text{ m sec}^{-1}$.

Figure 10c. Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 72.33$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 1.6 \text{ msec}^{-1}$.

Figure 10d. Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 113.01$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 2.5 \text{ msec}^{-1}$.

Figure 10e. Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 226.02$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 5.0 \text{ msec}^{-1}$.

Figure 10f. Streamlines for $\chi = 6.15 \times 10^4$ and $Re = 452.04$, corresponding to $2r_d = 700 \mu\text{m}$ at $U = 10.0 \text{ msec}^{-1}$.

Figure 11. Axis ratio for $\chi = 6.15 \times 10^4$ and $0.32 \leq Re \leq 452.04$, corresponding to $2r_d = 700 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.

Figure 12. Position of the rear stagnation point, z_{s2} , for $\chi = 6.15 \times 10^4$ and $0.32 \leq Re \leq 452.04$, corresponding to $2r_d = 700 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.

Figure 13a. Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 0.54$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 0.007 \text{ msec}^{-1}$

Figure 13b. Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 23.25$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 0.30 \text{ msec}^{-1}$.

Figure 13c. Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 46.49$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 0.60 \text{ m sec}^{-1}$.

Figure 13d. Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 123.99$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 1.6 \text{ msec}^{-1}$.

Figure 13e. Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 193.77$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 2.5 \text{ msec}^{-1}$.

Figure 13f. Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 387.47$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 5.0 \text{ msec}^{-1}$.

Figure 13g. Streamlines for $\chi = 1.05 \times 10^5$ and $Re = 774.93$, corresponding to $2r_d = 1200 \mu\text{m}$ at $U = 10.0 \text{ msec}^{-1}$.

Figure 14. Axis ratio for $\chi = 1.05 \times 10^5$ and $0.54 \leq Re \leq 774.93$, corresponding to $2r_d = 1200 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.

Figure 15. Position of the rear stagnation point, z_{s2} , for $\chi = 1.05 \times 10^5$ and $0.54 \leq Re \leq 774.93$, corresponding to $2r_d = 1200 \mu\text{m}$ with $0.007 \text{ msec}^{-1} \leq U \leq 10.0 \text{ msec}^{-1}$.

Figure 16. Axis ratio contours for water in air in the Re - We plane. $\bullet \alpha = 1.01$; $\cdot \alpha = 1.001$; $\blacksquare \alpha = 1$; $\blacktriangle \alpha = 0.95$; $\blacktriangledown \alpha = 0.9$; — falling water drops.

Figure 17. Axis ratio contours for water in air in the Re - Ca plane. $\bullet$ $\alpha = 1.01$; $\cdot$ $\alpha = 1.001$; $\blacksquare$ $\alpha = 1$; $\blacktriangle$ $\alpha = 0.95$; $\blacktriangledown$ $\alpha = 0.9$; — — falling water drops.

Figure 18a. Terminal velocity of falling water drops in air as a function of drop diameter.

Figure 18b. Reynolds numbers of falling water drops in air as a function of drop diameter.

Figure 19. Axis ratio for falling water drops in air as a function of drop diameter.

Figure 20. Normalized surface area for falling water drops in air as a function of drop diameter.

Figure 21a. Equatorial (●) and maximum (■) liquid-side tangential velocities for falling water drops in air as a function of drop diameter. (♦) indicates the measured value of Pruppacher and Beard (1970) for $2r_d = 710 \mu\text{m}$.

Figure 21b. Normalized equatorial (●) and maximum (■) tangential velocities for falling water drops in air as a function of drop diameter.

Figure 22a. Streamlines and shape of falling water drop in air with $Re = 0.19$ ($2r_d = 50 \mu\text{m}$).

Figure 22b. Streamlines and shape of falling water drop in air with $Re = 1.46$ ($2r_d = 100 \mu\text{m}$).

Figure 22c. Streamlines and shape of falling water drop in air with $Re = 8.67$ ($2r_d = 200 \mu\text{m}$).

Figure 22d. Streamlines and shape of falling water drop in air with $Re = 21.80$
($2r_d = 300 \mu\text{m}$).

Figure 22e. Streamlines and shape of falling water drop in air with $Re = 40.52$
($2r_d = 400 \mu\text{m}$).

Figure 22f. Streamlines and shape of falling water drop in air with $Re = 64.61$
($2r_d = 500 \mu\text{m}$).

Figure 22g. Streamlines and shape of falling water drop in air with $Re = 93.90$
($2r_d = 600 \mu\text{m}$).

Figure 22h. Streamlines and shape of falling water drop in air with $Re = 167.93$
($2r_d = 800 \mu\text{m}$).

Figure 22i. Streamlines and shape of falling water drop in air with $Re = 213.00$
($2r_d = 900 \mu\text{m}$).

Figure 22j. Streamlines and shape of falling water drop in air with $Re = 263.99$
($2r_d = 1000 \mu\text{m}$).

Figure 22k. Streamlines and shape of falling water drop in air with $Re = 386.65$
($2r_d = 1200 \mu\text{m}$).

Figure 221. Streamlines and shape of falling water drop in air with $Re = 544.17$
($2r_d = 1400 \mu\text{m}$).

Figure 22m. Streamlines and shape of falling water drop in air with $Re = 640.07$
($2r_d = 1500 \mu m$).

Figure 23. Axis ratio as a function of Reynolds number for water drops in air ($2r_d = 100\mu\text{m}$) at radius ratios $r_d/r_t = 0.1$ ($\blacksquare$), 0.2 ($\bullet$), and 0.5 ($\blacktriangledown$).

Figure 24a. Axis ratio contours for model fluid pair of Dandy and Leal in the Re - We plane.
 • $\alpha = 1.2$; ■ $\alpha = 1$; ▲ $\alpha = 0.95$; ▼ $\alpha = 0.9$.

Figure 24b. Axis ratio contours for model fluid pair of Dandy and Leal in the Re - Ca plane
 $\bullet$ $\alpha = 1.2$; $\blacksquare$ $\alpha = 1$; $\blacktriangle$ $\alpha = 0.95$; $\blacktriangledown$ $\alpha = 0.9$.

Figure 25a. Temporal variation of dimensional relative velocities for $2r_d = 100\mu\text{m}$.

Figure 25b. Dimensionless temporal variation of velocity ratios for $2r_d = 100\mu\text{m}$.

Figure 26a. Temporal variation of dimensional relative velocities for $2r_d = 400\mu\text{m}$.

Figure 26b. Dimensionless temporal variation of velocity ratios for $2r_d = 400\mu\text{m}$.

Figure 27a. Temporal variation of dimensional relative velocities for $2r_d = 700\mu\text{m}$.

Figure 27b. Dimensionless temporal variation of velocity ratios for $2r_d = 700\mu\text{m}$.

Figure 28a. Temporal variation of dimensional relative velocities for $2r_d = 1200\mu\text{m}$.

Figure 28b. Dimensionless temporal variation of velocity ratios for $2r_d = 1200\mu\text{m}$.

**Spectrometric System for Characterizing Drop and Powder Trajectories and Chemistry in
Reactive Flows**

Jerry C. Cabalo^{1,2†}, John Schmidt², Jost O. L. Wendt², and Alexander Scheeline^{1,*}

Submitted to the journal *Applied Spectroscopy*, March 1, 2002

Revised version submitted May 28, 2002

In press for publication in October, 2002 issue, Volume 56 Issue 10

**1 Department of Chemistry
University of Illinois at Urbana-Champaign
600 S. Mathews Ave.
Urbana, IL 61801**

**2 Department of Chemical and Environmental Engineering
University of Arizona
1133 N. Campus Dr.
Tucson, AZ 85721**

*** scheelin@scs.uiuc.edu**

† current affiliation; U. S. Army Research Laboratory, Aberdeen, MD

Abstract

An instrument for emission, fluorescence, and scattering diagnostics of a 22 kW gas/air thermal reactor is described. Z-pair parabolic mirrors provide diffraction-limited imaging in field center, with worst-case blur over a 12.8 mm field of view having a radius of 0.044 mm RMS. Either full-field filtered or transverse line dispersed viewing can occur simultaneously. Dispersion is achieved using a 2 m spectrograph f-matched to the feed optics. Examples of data show non-axisymmetric flow in a nominally laminar flow system, drop shapes *in situ*, and Mie scattering from soot.

Index Headings

Flame diagnostics, Planar Laser-induced Fluorescence, Spectroscopy in Harsh Environments, Imaging, Drop Vaporization

I. Introduction

Metal-bearing solutions and slurries can pose environmental hazards. Among the most acute of these hazards is the accumulation of radioactive wastes, held in underground steel tanks at locations such as Hanford, WA and the Savannah River Site at Aiken, SC [1-3]. Vitrification of radioactive wastes, either as glass logs [4] or cement [5] is the approach most actively being followed to sequester radionuclides over the millennia required for decay to negligible activity levels. An important step in preparation of vitrified material is removal of water and organic material, resulting in volume reduction. Among the ways to perform solvent removal, that simultaneously destroys organic matter, is thermal treatment. This process simply consists of spraying the waste into a high temperature ($T > 1800\text{K}$) reactor and adding powdered sorbent material. Water is vaporized, organics are oxidized to water and carbon dioxide, and metallic species oxidized. Scavenging of metal ions by kaolinite [6-9] prior to cooling and oxide formation is a promising technology for high efficiency collection of gas-phase radionuclides. Under optimized conditions, Destruction/Recovery Efficiencies (DRE's) of up to 99.99% of metal ions in an entering waste stream can be scavenged.

Considering the hundreds of millions of curies in the millions of gallons of waste [3], a DRE of 99.99% scavenging is entirely unacceptable. Understanding the cause of the 0.01% unscavenged fraction and devising means for its reduction are essential if thermal processing is to be used for nuclear waste treatment. Our hypothesis is that a small fraction of large ($>200\text{ }\mu\text{m}$ diameter), that is "rogue" drops originating from the input liquid stream or formed by coalescence in the reactor are responsible for the 0.01% unscavenged metals. These drops avoid hot zones in the reactor, resulting in either incomplete vaporization or vaporization in a zone with insufficient temperature to vaporize the metal contents. The metals form small particulates

that easily circumvent particle traps such as filters and cyclones [10]. Drop dynamics in analytical flames and plasmas has been studied for many years, including work by Hieftje (e.g. [11-13]), Farnsworth [14], and Olesik (e.g. [15-18]). To test the rogue drop hypothesis requires the ability to generate drops, both as sprays and as monodisperse streams, to measure drop size as a function of position, to measure drop and gas-phase temperature, and to observe speciation in the reactor including free atoms, small molecules, and soot. With the exception that a lack of a tunable laser prevented observation of free atoms, the apparatus reported here is capable of all these measurements. Drop generation is by use of an electronically-driven oscillating piezoelectric bimorph [10-11]. Temperature measurement within drops is based on exciplex fluorescence [19-25]. While we had hoped to measure soot temperature via laser-induced incandescence (LII) [26-28], the dispersion of the available spectrograph is more appropriate for atomic or molecular line/band emission rather than the LII continuum.

We now describe the flame diagnostics instrument and give examples of its use.

II. Design Principles

To have freedom from chromatic aberration and because of the success of all-reflective spatial and temporal resolution spectrometric systems in recent years, only reflective focusing elements were employed. The only transmissive components are windows in the sides of the reactor and one beam splitter.

The excitation laser beam was focused to a sheet illuminating a plane passing through the axis of the cylindrical reactor (Figure 1). A cylindrical mirror, dielectric-coated for maximum reflectivity at 308 nm, converted the rectangular (24 mm by 6 mm) beam from the excimer excitation laser to a 50 mm high, 1.6 mm thick illumination sheet. The central plane of this sheet is the object plane for the observation optics.

Stigmatic imaging was based on the work of Goldstein and Walters [29] as later implemented by Klueppel *et al.* [30], Hsu *et al.* [31], Scheeline *et al.* [32], and Scheeline *et al.* [33]. In this arrangement, images are relayed from point to point using parabolic mirrors, illuminated off-axis. Mirrors of nearly identical focal length are used in Z-pairs, so that each pair has no third-order coma and a controlled amount of astigmatism. Parabolic figure guarantees freedom from first order spherical aberration. By orienting at least one mirror pair perpendicular to one or more other mirror pairs, the astigmatism generated in one part of the optical train is compensated by equal astigmatism of opposite sign generated elsewhere in the train. The result is imaging with nearly-diffraction-limited performance, negligible vignetting, and no chromatic aberration. Image degradation away from the center of the field of view has been little discussed previously, though illustrated when this scheme was used in the construction of an echelle spectrometer [33]. In contrast to most previous implementations of this design, closed-form approximations in the placement of optics have been supplemented by ray traces using *Zemax* (Focus Software, Tucson, AZ).

Minimal optical aberrations and maximum throughput are necessary in this system. Image fidelity is required for planned studies of drop deformation as a function of reactor flow and the effect of such deformation on drop trajectory. For the optical system described here, a 200 μm drop image will be 8 pixels in diameter. If distortion changes the measurement by one pixel, then the apparent dimensional error introduced is great than 10%. Maximum throughput is necessary to image potentially faint fluorescence signals. Combustion gases, particulates, and the high $f/\#$ imposed by the geometric constraints of access ports will attenuate signal, and an efficient optical train is necessary to mitigate this problem for adequate signal to noise.

The downflow reactor being studied is 6 m tall, with a ring of four access ports 4.75" (12.1 cm) below the burner head and then incomplete rings of 3 ports (missing port on the side of the reactor away from the observation optics) every 12" (305 mm) thereafter. The top three ports were available for observation, though the optical design and all data reported here were for observations through the top-most port, where drop vaporization would be minimal. Because light is nearly collimated as it descends parallel to the reactor axis, observation at lower ports is feasible, provided only that there is no interference between collimating and focusing optics, nor between folding mirrors (should observation be desired below the plane of the optics shown in Figure 1, the beam extraction/collimation and beam focusing/folding mirrors could simply be inverted). Subsequent measurements have used lower ports, requiring only that the Lucite beam covers be modified. The system is robust against vertical vibration.

For some experiments, either wavelength-integrated measurements or measurements limited only by bandpass filters are desirable. For other measurements, sub-nanometer resolution as most conveniently provided by a scanning spectrograph is desirable. The optical system was designed with two focal planes (Figure 1), one of which used a 2 m Czerny-Turner spectrograph for dispersion (Minuteman Laboratories, Acton, MA), the other of which simply focused an image onto an intensified CCD camera. Because of the 10.92 mm astigmatism of the spectrograph, different astigmatism compensation optics were designed for the two focal planes. The initial image transfer was from a single Z-pair of mirrors; just beyond the astigmatic focal region for this pair was located a UV beam splitter. While we currently only own a single CCD, this design insured both that simultaneous monitoring at the two focal planes would be possible and that both focal planes could observe the same volume simultaneously.

In contrast to typical spectroscopic work, the optical system resided in a lab that can most succinctly be described as "dirty." Coal dust from experiments and infiltrating sand particles from the Arizona desert are frequent specimens in the reactor bay. UV laser optics are highly susceptible to damage from surface dust, yet dust was a concomitant of nearly all experiments. We thus covered the optical system with Lucite (which also served to enhance eye safety, as polymethylmethacrylate absorbs 308 nm laser light), and pumped dry HEPA-filtered air into the enclosure. Despite months of experiments on coal dust combustion taking place on both the reactor in which we observed drop dynamics and in an adjacent reactor, which together left a thick coating of dust on the outside of the spectrograph and Lucite box housings, the optical path remained free of detectable dust and the mirrors never suffered damage.

The only excitation yet employed on this apparatus is the 308 nm XeCl laser band (Lambda Physik COMPex 201, Ft. Lauderdale, FL). Ultraviolet wavelengths were chosen so that signals would be well away from the blackbody continuum emitted by the reactor walls. Pulsed illumination assisted in temporal selection against continuum while assisting in obtaining strong signals from single drops. Signal-to-noise ratio calculations suggested that illumination at over 10 mJ per pulse would be required to obtain adequate LIF, LII, and Mie scattering signals. Budget dictated that a tunable laser with this power was out of the question. The only laser meeting all these constraints is an excimer laser. The desire to excite both OH (for flame temperature measurement) and some convenient metal atom (Al at 308.4 nm or Cu at 307.47 nm) led to our choice of XeCl. We plan to obtain a tunable dye laser in the future. The only components that must be changed to accommodate tunable operation are the mirrors that relay and focus the laser beam to the mid-plane of the reactor.

III. Components, Assembly, and Characterization

Optical components are summarized in Table I, with off-axis angles shown in Table II. A reviewer noted that the Minuteman 2 m spectrograph is uncommonly used in flame diagnostics, but that the Jarrell-Ash 0.25 m Ebert monochromator/spectrograph is widely employed. The setup using such an instrument is that shown in the tables except that the lower astigmatism of the short focal length Ebert mount means that the off-axis angle for the over/under mirror pair is 3.78° instead of 2.55° . This translates the upper 1000 mm f.l. mirror 280 mm closer to the lower mirror, pushing the last 45° folding mirror a similar distance away from the reactor. Because the Ebert's mirror is illuminated off-axis, the computed ultimate spatial resolution is poorer (geometric spot diameter in field center $50\text{ }\mu\text{m}$) than in the system we built and characterized.

Most planar laser-induced fluorescence apparatus use cylindrical lenses to focus the incident laser beam. We chose to use a cylindrical mirror (Harold Johnson Optical Labs, Gardena, CA) as we needed a focal length of 50", a distance not commonly available and also wavelength-dependent in a transmitting optic. The high effective $f/\#$ of any focusing optic illuminated by the nearly-collimated beam of an excimer laser means that a spherical surface was adequate to our needs. The Lambda Physik COMPEX 205 XeCl laser has a nominal exit beam 24 by 6 mm with divergence of 3 mrad and 1 mrad respectively. Given the relationship for diffraction-limited beam width, $f\lambda = w x_{\min}$, where f is the distance from the focusing aperture to the beam waist, λ the laser wavelength, w the half-width of the beam at the focusing optic, and $x_{\min}$ the full width of the focused beam waist is $75\text{ }\mu\text{m}$, significantly smaller than the 1.6 mm sheet thickness at our observation zone computed via ray-tracing. Beam divergence fluctuates from shot to shot, making precise compensation for beam divergence a chimera. If beam divergence were a rigorously repeatable parameter, a nearly diffraction-limited beam might be obtained either by

accounting for the beam divergence (which moves the nominal beam waist ~420 mm beyond the reactor center using the dimensions shown in Table I) or choosing a mirror with a shorter focal length. The comparatively thick illumination sheet relaxes the precision with which injected drops must be aimed, and insures illumination of all of even large drops. In addition, such defocusing lowers peak power density, reducing the incidence of unintentional laser-induced breakdown (LIBS) [34-37]. While we saw no evidence of LIBS, there is sufficient power in a 400 MW 308 nm laser pulse that, if more tightly focused, such processes would be anticipated.

The focusing components of the observation optics all employed off-axis-illuminated, on-axis parabolic mirrors. The 600 mm and 1000 mm feed optics for the non-dispersed focal plane and spectrograph, respectively, were those previously used in a time-resolved, space-resolved spectrometric system used for observing spark discharges and theta pinches³². The mirrors were remounted so that the off-axis angles were those listed in Table 2. The down-link from the reactor to the main assembly of feed optics used newly obtained mirrors (Astronomically Xenogenic Enterprises, (AXE) Tucson, AZ) of 1270 ± 1 mm focal length. Mirrors were aluminized and MgF_2 coated for optimum reflectance at 308 nm. Ray traces indicated that the expected image blur at both spectrograph and non-dispersed focal planes would be less than the 25 micron pixel size at the intensified CCD face-plate. In the center of the observation field, this was indeed the case. At the edges of the observation field (6.4 mm laterally and vertically, or 8.8 mm diagonally from image center), coma was evident. The ray trace result for a point object, both in the center and at the corners of the viewed field, appears in Figure 2.

Windows to admit the laser beam to the reactor were anti-reflection coated on the outside (no coating was warranted on the inside, as reactive gases would consume these coatings over time). A nitrogen purge behind the windows helps keep them from becoming soot-covered. The

observation beam splitter is a 6 mm thick dielectric-coated quartz substrate, tilted at 45° to the incoming optical axis. It generates lateral chromatic aberration ($n(200\text{ nm}) = 2.404$, $n(800\text{ nm}) = 2.112$, so that beam offset vs. 308 nm ($n = 2.207$) ranges from -0.083 mm to $+0.247\text{ mm}$), but in no instance shifts the field of view of the spectrograph by more than $\frac{1}{4}\text{ mm}$ from that of the non-dispersed image.

Stray light from the laser could be both an eye hazard and a threat to the photocathode of the intensified CCD camera. An efficient beam dump is thus essential. Stacked razor blades, with the blade edge parallel to beam polarization [38], proved to be sufficient. The beam dump was recessed in an access port diametrically opposite the admission port for the laser. The flame igniter also used the same port, so placement of the beam dump could only occur after the combustor was ignited.

Gated detection is essential for several reasons. First, while the optics bench is covered with black cloth, stray room light contributes some signal if long integrations are used. Second, while observations are typically in the mid-UV, where 1800 K blackbody continuum is negligible, only broadband filters have been used to date. Time gating enhances the signal-to-background ratio by synchronizing detector response to laser firing. Time gating could be used to differentiate fluorescence, laser-induced incandescence, and laser-induced plasma emission from scattering, but this has not been successfully observed to date. The intensifier was chosen for optimal ultraviolet response. The IMAX-512 has the image intensifier pixels on 25 micrometer centers; the output bonded fiber optic array tapers to the 18 micron CCD pixels (Thomson, $5 \times 10^5\text{ e}^-$ full well capacity, 16 bit ADC). On/off gating ratio was not measured, but is claimed to be $>10^4$. Thermo-electric cooling was adequate; dark current was not significant in any experiments reported here.

Many mechanical components were fabricated at the University of Illinois School of Chemical Sciences Machine Shop and shipped to the University of Arizona as a flame spectroscopy toolkit. The University of Arizona Department of Chemical and Environmental Engineering Machine Shop was employed to fabricate the Lucite housings, gas handling system, reinforcements to stabilize the cart holding the excimer laser, and an assortment of other components not anticipated in the original design. The combination of the large capacity at Illinois with the contiguous access to both skilled personnel and equipment at Arizona were necessary for the successful completion of the instrument. In a field not noted for research at remote facilities, managing instrument completion proved to be an exercise in management and cooperation on an unfamiliar scale.

Both commercial and in house software was used for data acquisition and instrument control. Image data from the Princeton Instruments digital camera was recorded using *Winspec* software written by the manufacturer. Computer control of the spectrograph was achieved using a Computer Boards CIO-CTR05 digital I/O card with C⁺⁺ software to pulse the stepper motor. Spectral data was recorded using either the Princeton Instruments CCD camera or a photomultiplier tube. Again, the commercial software package *Winspec* was used in conjunction with the ICCD camera. Data from the photomultiplier tube was digitized and integrated using a Tektronix TDS 220 digital oscilloscope controlled with C⁺⁺ software.

Monodisperse streams of large drops were formed by a specially designed vibrating orifice drop generator. This system is a variation of the system used by Hanlon and Melton [39]. The generator body consisted of a brass ring with a diametrically-opposed nozzle assembly and feed tube. The two open ends of the ring were sealed with piezo-electric buzzer units (Radio Shack, model 273-064) driven by a Hewlett Packard 214B square wave generator. The nozzle

assemblies were formed from ruby orifices with diameters between 190 and 254 μm (Byrd Scientific), fixed at the end of a conical brass nozzle, which in turn was brazed to the brass ring. The feed tube and the nozzle assembly formed the axis of the generator.

The generator could be operated in two modes: vibrating-orifice-drop-generator mode (VODG) and drop-on-demand mode (DOD). VODG mode was capable of forming drop arrays with drop diameters ranging from 350 μm to 750 μm by vibrating the assembly at frequencies ranging from 1 kHz to 20 kHz. Liquid was fed to the drop generator from a sealed vessel pressurized with compressed air up to 10 psig, though the typical operating pressure was 5 psig or less. The monodisperse drop stream was formed when the buzzer units were synchronously vibrated at the proper frequency. At frequencies less than 1 kHz, no monodispersity was observed, and at frequencies higher than 15 kHz monodispersity was lost as drops coagulated due to decreased drop spacing. In DOD mode, only a light backing pressure was used in the reservoir, and this was achieved by maintaining the liquid level a few millimeters above the nozzle opening. Drop sizes of 300 μm up to about 700 μm were available at repetition rates up to 50 Hz. However, DOD generation proved to be impractical in the existing furnace due to extreme sensitivity to the height of the liquid level in the reservoir. Also, the liquid tended to bead up around the nozzle, thus preventing drop generation. This problem is easily surmounted by pulsing the reservoir pressure, but without the ability to directly observe the nozzle tip, this solution is impractical. In addition, the low duty cycle of this drop generation mode (~50 Hz and less) in comparison to VODG mode (1-15 kHz) made synchronization with the laser and camera very critical. It was very difficult to achieve stable drop generation, proper alignment between the drop stream and the observation volume, and proper synchronization simultaneously. Thus, all experiments were performed in VODG mode.

The drops were injected into the furnace through a specially designed gas/air burner. The gas/air premix entered the combustor via an annulus with an outer diameter of 52.76 mm (2 5/64") and an inner diameter of 42.85 mm (1 11/16"). The drop streams were injected through a hole in the center of the annulus and thus through the centerline of both the furnace and the burner. Due to the sensitivity of the piezo-electric elements to heat, the burner was designed to maintain a high flow rate of cooling water through the head of the burner and around the drop generator nozzle assembly. Even at the maximum heat load attainable, the tip of the aerosol generator was only warm to the touch.

IV. Results and Discussion

To date, work has focused on the use of filtered full-field images to characterize drop trajectories and sooting behavior. Spectrographic/high resolution data have not been useful for single laser firings, as no atomic or diatomic molecular species present in the reactor absorb and efficiently fluoresce at 308 nm. The $\text{OH}^* X^2\Pi, \rightarrow A^2\Sigma^+$ band overlaps with excimer emission. The band head at 306.36 nm is below the low-wavelength end of the excimer bandwidth, but higher ro-vibronic states overlap portions of the laser spectrum. Typical ro-vibrational Doppler linewidth at 1500 K (the highest temperature obtained from the gas-air flame) is ~ 2 pm. Because the laser must traverse ~ 50 mm of hot gas prior to reaching the observation window, and because the flame front is invisible, a combination of low OH concentration, pre-filter effects, limited overlap between excimer emission and populated OH state absorption, and low $f/\#$ precluded observation of this radical. Similarly, while Al I has a strong line at 308.4 nm, the low temperature and high oxygen concentration (even under relatively rich flame conditions) resulted in negligible Al free atom fraction and no observable emission or fluorescence. A dye

laser clearly would have the spectral radiance and tunability to allow observation of all relevant flame and drop solute elements and radicals.

We thus confine discussion to observations of drops, gas flows, and soot. Drops of either water or diesel fuel were used, as noted for each experiment. An initial characterization of the instrument was to demonstrate optical fidelity, throughput, and freedom from stray light by imaging Mie scattering from 5% acetone/water drops of known size. Pure water drops focused the laser light and appeared as bright spots just a few pixels across, while the rest of the drop appeared dark. Complete visualization of the drops was accomplished by blocking the scattered light with a colored glass filter and imaging the fluorescence of the acetone tracer instead. A bright spot appears where each drop focused the laser light. Drop shapes vary from spherical to flattened. The acetone tracer even fluoresced at high flame temperatures, allowing visualization of drop under combustion conditions. No tracer was required with diesel drops because of naturally-occurring aromatic hydrocarbons that are naturally present in diesel fuel and are strongly pumped at 308 nm, fluorescing strongly as shown in Figures 3 and 4.

The drop sizing capability of the apparatus was investigated by comparing the size measured by the apparatus with known drop sizes. A drop stream of the water/acetone solution was first captured in a beaker and weighed; given the known number of drops and density of water, the average mass per drop and thus drop diameter for spherical drops was known (correction for the density change caused by acetone is negligible for our circumstances). The stream was then passed through the center of the reactor (no fuel, room temperature). Intensifier gain was set to 100 (maximum is 256) and the camera was filtered with a Melles-Griot Colored Glass BG-25 filter and a WG-320 cut-off filter, both 2 mm thick.. Results are shown in Figure 3, with data tabulated in Table III. In all cases, optically-determined sizes are less than those expected,

typically by approximately 1 pixel or 5%. Considering that some evaporative loss is expected and that optical magnification is calculated to be 1.003, this is acceptable. In addition to drop sizing, drop imaging was quite effective in determining drop shapes. Smaller drops ($d < 500 \mu\text{m}$) tended to be spherical, and larger drops tended to be slightly flattened. Drop shape and size are extremely important for determining drop drag coefficients that help predict the penetration of drops into the combustor. The drop size and shape also affect the transport of vapor material away from the drop, which will be the subject of future investigation.

At sufficiently high spray rates, drop collisions and coagulation can be seen (Figure 4). Drop growth as well as vaporization can thus be observed, such that if rogue drops are due to in-flame agglomeration, this will be observable. The fate of diesel drop groups was observed at three points positioned along the centerline of the furnace 12.1 cm, 42.6 cm, and 73.0 cm downstream from the burner. At low gas flow rates, drop groups tended to remain intact even down to the third port, with no coagulation evident. However, as the gas flow was increased, the drop stream was broken up, the drops were observed to form clump like formations, and coagulation was observed at the second and third ports. Except at the highest flow rates, the drop groups were not broken up at the first port. We attribute the breakup of drop formations to turbulence, since turbulence is expected near the burner because the Reynold's number within the burner ranged from $Re=13000$ to $Re=20000$, which are clearly in the turbulent regime. The flow was expected to laminarize as the annulus in the burner opened out to the bore of the combustor, where the Reynold's number was calculated to be less than 250. Except at the lowest flow rates, drops were rarely observed at the third port, and these drops no longer remained in linear formation.

A statistical analysis of the coagulation data was only possible for that obtained at the first port, due to the limited field of view of the instrument. Given that the active area of the ICCD

camera was 12.5×12.5 mm, the 1:1 magnification of the optical system and the laser beam width, the observable volume within the combustor measured $12.5 \text{ mm} \times 12.5 \text{ mm} \times 1.6 \text{ mm}$. As a result, it was difficult to completely characterize drop trajectories except at the first port, due to drop travel outside the observation volume. However, it was clear that for large drops that the path of the drops were not greatly affected by turbulence until several diameters of the burner annulus downstream.

Another issue of importance for thermal destruction of liquid waste is the gas phase transport of material originating from the liquid drops and possible uptake by sorbent particles. This was investigated by observing the transport of PAH from diesel drops, as shown in Figure 5. With the Schott BG-25 and WG-320 filters, the camera was optimized for imaging light in the range of 350 nm to 450 nm, the emission wavelength range for PAH. The most intense PAH signal arises from the liquid phase, where the strong attenuation of laser light through the thickness of the drops appears as the signal rapidly decays from the right to the left in Figure 5A. Fluorescence from the gas phase PAH in a gas phase concentration map clearly shows the transport of vapor away from the drop array.

Figure 6 shows the radial cross sections of PAH fluorescence from the middle of the drop stream to the edge of the observable volume. The lower curve is the signal through the saddle point between drops, and the upper curve is a cross section through the middle of a drop. The signal through the saddle point decreases in an exponential fashion until it reaches a cusp, which incidentally is where this curve intersects the cross section through the drop. The position of this intersection point does not change with respect to drop injection velocity. This can be explained by the fact that the decay in PAH signal is a combination of diffusive and convective transport away from the drop stream and the thermal degradation of the PAH. Material vaporizing from

the drop stream should experience rapid heating from the diesel wet bulb temperature to ~1700 K (measured with a thermocouple at the first observation port). Thus, thermal degradation should be a dominant factor in the decay of PAH signal. Future work will concentrate on separating the contributions of chemical degradation and transport in order to quantify transport properties. With a tunable laser radiation source, the transport properties of various materials such as heavy metals and their oxides whose properties are not completely known can be directly measured under combustion conditions.

In the process of thermal waste destruction, as well as in combustion processes, small particle formation is important. In the case of metal-bearing waste, refractory metals released into the gas phase readily form small particles. In the case of combustion, soot formation is also an important process. Thus, it is important that this system also have the capability of detecting small particles. Soot was imaged, as shown in Figure 7. A UG-11 filter was used to block much of the visible spectrum. Though the CCD camera does not have the resolution to image individual particles less than 25 μm in size, the scattered light intensity was much more intense than the fluorescence signals, so much so that even at the minimum gain setting on the camera intensifier signals from drops would almost saturate the camera. The apparatus is capable of detecting zones containing sufficient concentrations of particles. Soot appeared in clouds surrounding the drop streams. Only for lean conditions did soot appear to be forming in the wake of individual drops. Otherwise, the soot appeared to be formed from the diesel vapor from previous drops. Some of the images showed clumping of the soot. Soot was also helpful in visualizing the motion of the gas surrounding the drop stream. At the second and third port, the soot also revealed turbulent eddies, as well as how diesel drops also interacted with the

surrounding gas. It is clear from Figure 7 that even at port 2 the drops pulled soot material into their wakes when they were still traveling faster than the surrounding gas.

V. Conclusion

A new, high fidelity imaging apparatus has been constructed for the observation of drop dynamics and vapor transport properties in multi-kilowatt thermal reactors. The apparatus is capable of optically determining the size and shape of drops for the determination of drag coefficients. Important events such as drop coagulation can be observed. In addition, suspended and vapor phase material, such as soot and PAH vapor surrounding the drops that pertain to gas phase transport, have been imaged. Soot images showed the interaction between the drops and the surrounding combustion gases as the drops ploughed through. The instrument was also shown to be capable of recording emission spectra within the combustor, though detection of sodium 589 nm spontaneous emission blank in distilled water required ~ 1 s ungated integration.

Future studies will more thoroughly investigate drop trajectories with a modified burner that guarantees a well characterized axisymmetric flow, which is necessary for comparing with fluid dynamics models. In addition, with the addition of a tunable laser, PLIF imaging will be used to investigate the transport and combustion of materials arising from the drop arrays.

Acknowledgement

This work was supported in part by the United States Department of Energy Environmental Management Science Program, grant DE-FG07-97-ER14837. In addition, support from the University of Illinois Research Board is gratefully acknowledged. Fabrication and engineering by and discussion with the University of Illinois School of Chemical Sciences Machine Shop (particularly William Knight, Roger Smith, Roy Walton), University of Illinois School of Chemical Sciences Electronics Shop, Arne J. Pearlstein, William P. Linak, Sheldon Davis and Lorenzo Lujan are also greatly appreciated.

References Cited

1. C. W. Terrell, "High Level Waste Management, Processing, and Vitrification at the Savannah River Site," *Nucl. Mater. Manage.*, **23**, 233-237 (1994).
2. G. Zorpette, "Confronting the Nuclear Legacy – Part II. Hanford's Nuclear Wasteland," *Sci. Am.* **274**(5), 88-97 (1996).
3. T. L. Stewart, "Overview of U. S. Radioactive Tank Problem," Book of Abstracts, 214th ACS National Meeting, Las Vegas, NV I&EC-055 (1997).
4. S. A. Tollison and S. M. Finger, "Glass – the Ultimate Waste Form," *Radiat. Prot. Manage.* **14**, 45-49 (1997).
5. M. L. D. Gougar, B. E. Scheetz, and D. D. Siemer, "A Novel Waste Form for Disposal of Spent-nuclear-fuel Reprocessing Waste: a Vitrifiable Cement," *Nucl Technol.* **125**, 93-103 (1999).
6. S. B. Davis, J. O.L. Wendt, and W. P. Linak, "Interactions between Lead Vapor and Sorbents at High Temperatures," *Chem. Phys. Processes Combust.* 157-159 (1999).
7. S. B. Davis, T. K. Gale, and J. O. L. Wendt, "Competition for Sodium and Toxic Metals Capture on Sorbents," *Aerosol Sci. Technol.* **32**, 142-151 (2000).
8. S. B. Davis and J. O. L. Wendt, "Quantitative Analysis of High Temperature Toxic Metal Sorption Rates Using Aerosol Fractionation," *Aerosol Sci. Technol.* **33**, 536-543 (2000).
9. S. B. Davis and J. O. L. Wendt, "Mechanism and Kinetics of Lead Capture by Kaolinite in a Downflow Combustor," *Proc. Combust. Inst.* **28**(Pt. 2), 2743-2749 (2000).
10. J. A. Mulholland, R. K. Srivastava, J. O. L. Wendt, S. R. Agrawal, and W. S. Lanier, *Combust. Flame*, **86**, 297-310 (1991).

11. N. C. Clampitt and G. M. Hieftje, "Mechanism of Desolvation of Sample Droplets in Flame Spectrometry," *Anal. Chem.* **44**, 1211-1219 (1972).
12. J. G. Shabushnig and G. M. Hieftje, "A Novel Device for the Accurate Dispensing of Small Volumes of Liquid Samples," *Anal. Chim. Acta*, **126**, 167-174 (1981).
13. A. G. Childers and G. M. Hieftje, "Measurement of Solute Vaporization Rates in an Analytical Flame by Laser-Light Scattering," *Anal. Chem.* **65**, 2761-2765 (1993).
14. A. C. Lazar, and P. B. Farnsworth, "Characterization of an Inductively Coupled Plasma with Xylene Solutions Introduced as Monodisperse Aerosols," *Anal. Chem.* **69**, 4932-4939 (1997).
15. J. W. Olesik, "Investigating the Fate of Individual Sample Droplets in Inductively coupled Plasmas," *Appl. Spectrosc.* **51**, 158A-175A (1997).
16. J. W. Olesik, J. A. Kinzer, and G. J. McGowan, "Observation of Atom and Ion Clouds Produced from Single Droplets of Sample in Inductively coupled Plasmas by Optical Emission and Laser-induced Fluorescence Imaging," *Appl. Spectrosc.* **51**, 607-616 (1997).
17. S. E. Hobbs, and J. W. Olesik, "The Influence Of Incompletely Desolvated Droplets and Vaporizing Particles on Chemical Matrix Effects in Inductively Coupled Plasma Spectrometry: Time-Gated Optical Emission and Laser-Induced Fluorescence Measurements," *Spectrochim. Acta, Part B*, **52B** 353-367 (1997).
18. I. I. Stewart, and J. W. Olesik, "Time-resolved Measurements with Single Droplet Introduction to Investigate Space-Charge Effects in Plasma Mass Spectrometry," *J. Am. Soc. Mass Spectrom.* **10**, 159-174 (1999).

19. L. A. Melton, "Spectrally Separated Fluorescence Emissions for Diesel Fuel Droplets and Vapor," *Appl. Opt.* **22**, 2224-2226 (1983).
20. A. M. Murray and L. A. Melton, "Fluorescence Methods for Determination of Temperature in Fuel Sprays," *Appl. Opt.* **24**, 2783-2787 (1985).
21. H. E. Gossage, and L. A. Melton, "Fluorescence Thermometers Using Intermolecular Exciplexes," *Appl. Opt.* **26**, 2256-2259 (1987).
22. S. K. Nickle, and L. A. Melton, "Fluorescence Lifetime and Quenching Rates for N,N,N',N'-tetramethyl-p-phenylenediamine in the Vapor Phase," *Appl. Spectrosc.* **43**, 1406-1409 (1989).
23. L. A. Melton, "Exciplex-based Vapor/Liquid Visualization Systems Appropriate for Automotive Gasolines," *Appl. Spectrosc.* **47**, 782-786 (1993).
24. F. Bai and L. A. Melton, "High-temperature, Oxygen-resistant Molecular Fluorescence Thermometers," *Appl. Spectrosc.* **51**, 1276-1280 (1997).
25. Q.-Z. Lu and L. A. Melton, "Measurement of Transient Temperature Field within a Falling Droplet," *AIAA J.* **38**, 95-101 (2000).
26. L. A. Melton, "Soot Diagnostics Based on Laser Heating," *Appl. Opt.* **23**, 2201-2208 (1984).
27. R. T. Wainner, *An Analytical and Quantitative Analysis of the Laser-Induced Incandescence of Soot*, Ph.D. Thesis, Georgia Institute of Technology (1999),
28. P. O. Witze, S. Hochgreb, D. Kayes, H. A. Michelsen, and C. R. Shaddix, "Time-resolved Laser-induced Incandescence and Laser Elastic-scattering Measurements in a Propane Diffusion Flame," *Appl. Opt.* **40**, 2443-2452 (2001).

29. S. A. Goldstein and J. P. Walters, "A Review of Considerations for High-fidelity Imaging of Laboratory Spectroscopic Sources. Part I," *Spectrochim. Acta*, **31B**, 201-220 (1976).
30. R. J. Klueppel, D. M. Coleman, W. S. Eaton, S. A. Goldstein, R. D. Sacks, and J. P. Walters, "A Spectrometer for Time-gated, Spatially-resolved Study of Repetitive Electrical Discharge," *Spectrochim. Acta*, **33B**, 1-30 (1978).
31. W. H. Hsu, M. A. Sainz, and D. M. Coleman, "An Aberration-Corrected Time- and Spatially-Resolved Spectrometer for Studies of Transient Discharges," *Spectrochim. Acta*, **44B**, 109-121 (1989).
32. Alexander Scheeline, Gregory J. Kamla, and M. J. Zoellner, "Electron Concentration Measurement in the High Voltage Spark Using Stark Broadening of H β Emission," *Spectrochim. Acta*, **39B**, 677-691 (1984).
33. A. Scheeline, C. A. Bye, D. L. Miller, S. W. Rynders, and R. C. Owen, Jr., "Design and Characterization of an Echelle Spectrometer for Fundamental and Applied Emission Spectrochemical Analysis," *Appl. Spectrosc.* **45**, 334-341 (1991).
34. D. E. Lencioni, "Effect of Dust on 10.6 μ m Laser Induced Breakdown." *Appl. Phys. Lett.* **23**, 12-14 (1973).
35. D. E. Lencioni, "Laser Induced Breakdown for 1.06 μ m Radiation." *Appl. Phys. Lett.* **25**, 15-17 (1974).
36. J.-B. Zhang, W.-F. Hsieh, S.-C. Chen, and R. K. Chang, "Laser-induced Breakout and Detonation Waves in Droplets. I. Experiments." *J. Opt. Soc. Am. B*, **8**, 319-328 (1991).
37. J. C. Carls, Y. Seo, and J. R. Brock, "Laser-induced Breakout and Detonation Waves in Droplets. II. Model." *J. Opt. Soc. Am. B*, **8**, 329-336 (1991).

38. M. J. Zoellner and A. Scheeline, "Channel and Analyte Dynamics in the High Voltage Spark Discharge Using Raman, Fluorescence, and Emission Spectroscopies," *Appl. Spectrosc.* **41**, 943-954 (1987).
39. T. R. Hanlon and L. A. Melton, "Exciplex Fluorescence Thermometry of Falling Hexadecane Droplets," *J. Heat Transfer Trans. ASME*, **114** 450-452(1992).

Table I. Components Used in Fluorescence, Scattering, Emission Apparatus. All positions are referenced to the center of the observation point in the reactor when viewed through the top port, just below the combustor inlet. Axes are for a right-handed Cartesian system, with fluoresced or scattered light observed when directed along the x axis, laser entering along the +y axis.

Component	Description	Vendor	x (mm)	y (mm)	z (mm)
Excimer Laser	308 nm XeCl	Lambda Physik	159	1465.00	-1016.54
Folding Mirror 1	dielectric, 308 nm	Melles Griot, Irvine, CA	0	1465.00	-1016.54
Folding Mirror 2	dielectric, 308 nm	Melles Griot	0	943.57	-1016.54
Cylindrical Mirror	50" f.l. dielectric	Fabrication: Harold Johnson Optical Labs, Gardena, CA; Coating: Acton Research	0	943.57	477.07
Folding Mirror 3	3" Ø dielectric	Melles Griot	0	793.40	0
Reactor Entrance Window (outer surface)	2" diameter quartz, AR coated one side	CVI Laser Corp., Albuquerque, NM	0	730	0
Observation Point			0	0	0
Reactor Exit Window (outer surface)	2" diameter quartz, AR coated one side	CVI Laser Corp.	723.22	0	0
Folding Mirror 4	3" diameter Al mirror, MgF ₂ coating, 310 nm optimized	Melles Griot	793.65	0	0
Collimation Parabola 1	50" (1270 mm) f.l. f/15 parabola	Astronomically Xenogenic Enterprises, (AXE) Tucson, AZ	837.33	0	474.39
Collimation Parabola 2	50"	Same	837.33	0	-1422.41
Folding Mirror 5	3" Ø Al mirror	Melles Griot	903.61	0	-698.51
Beam Splitter		CVI Laser Corp, Albuquerque, NM	1485.24	0	-698.51
Folding Mirror 6	3" Al mirror	Melles Griot	1485.24	127	-698.51
Z-pair 1 Mirror 1	600 mm f.l. f/15 parabola	3B Optical Co.	1034.24	127	-698.51
Z-pair 1 Mirror 2	600 mm	Same	1866.08	254.7	-698.51
ICCD	IMAX-512 Fiber-optic coupled 512x512, 18 µm pixel	Roper Scientific	1266.07	254.7	-698.51
Z-pair 2 Mirror 1	1000 mm f.l. 4/15 parabola	3B Optical Co.	2455.72	0	-698.51
Z-pair 2 Mirror 2	1000 mm	Same	1602.12	0	-622.33
Folding Mirror 7	3" Al mirror	Melles Griot	2358.61	0	-622.33
Spectrograph entrance slit	2 m f.l. 1200 g/mm grating	Minuteman Labs, Acton, MA	2358.61	257.3	-622.33

Table 2. Mirror off-axis angles

Mirror	Off-axis angle
50" cylinder	3.00°
50" parabolas	3.00°
600 mm parabolas	4.364°
1000 mm parabolas	2.55°
2 m spectrograph collimator	2.71°
2 m spectrograph camera	3.25°

Table 3. Observed vs. computed drop diameter (see Figure 3).

Measured diameter (weighed drop stream)	Apparent diameter
405 μm	375 μm
511 μm	500 μm
606 μm	575 μm

Figure Captions

Figure 1. Optical Layout. Two planar folding mirrors direct the 308 nm, 25 ns 400 mJ beam to a cylindrical mirror that focuses the beam through a quartz window into the center of the reactor. The observation optics are orthogonal to the illumination optics, directing the fluoresced/emitted/scattered light to either a non-dispersed focal plane or to a 2 m spectrograph.

Figure 2. Images of point objects at center and corners of visual field (*Zemax* ray trace). Worst case resolution is 0.2 mm.

Figure 3. Water drops of known mean diameter, observed with a single excimer laser pulse through a 308 nm center, 2 nm bandpass filter, room temperature. Comparison of expected and observed diameters in Table 3.

Figure 4 Drop stream showing agglomeration of adjacent drops.

Figure 5 PAH fluorescence both in drops and in the atmosphere surrounding drop trajectories.

Figure 6 Cross sections of the PAH fluorescence in Figure 5. The ordinate axis position marks the midpoint of the drop array. Light line goes through drop; heavy line is midway between drops.

Figure 7 Image of scattered laser light from diesel drops passing through clouds of soot recorded at the second port. The soot material entrained in the drop wake indicates the high drop velocity with respect to the surrounding gases. Note that the drop acts as a lens and focuses laser light to a bright spot.

Figure 1. Optical Layout. Two planar folding mirrors direct the 308 nm, 25 ns 400 mJ beam to a cylindrical mirror that focuses the beam through a quartz window into the center of the reactor. The observation optics are orthogonal to the illumination optics, directing the fluoresced/emitted/scattered light to either a non-dispersed focal plane or to a 2 m spectrograph.

OBJ: -6.4000, 6.4000 MM

IMA: 6.407, 6.428 MM
FIELD 5

OBJ: -6.4000, -6.4000 MM

IMA: -6.402, 6.435 MM
FIELD 3

OBJ: 0.0000, 0.0000 MM

200.00

IMA: -0.000, -0.000 MM
FIELD 1

OBJ: 6.4000, 6.4000 MM

IMA: 6.402, -6.431 MM
FIELD 2

OBJ: 6.4000, -6.4000 MM

IMA: -6.397, -6.439 MM
FIELD 4

UNITS ARE MICRONS.

FIELD :	1	2	3	4	5
RMS RADIUS :	5.104	43.565	41.395	29.438	28.586
GEO RADIUS :	7.436	80.852	77.831	47.669	40.580
SCALE BAR :	200 MICRONS				

Figure 2. Images of point objects at corners of visual field (*Zemax* ray trace). Worst case resolution is 0.2 mm.

Figure 3. Water drops of known mean diameter, observed with a single excimer laser pulse through a 308 nm center, 2 nm bandpass filter, room temperature. Comparison of expected and observed diameters in Table 3.

Figure 4 Drop stream showing agglomeration of adjacent drops.

A

B

Figure 5 PAH fluorescence both in drops and in the atmosphere surrounding drop trajectories.

Figure 6 Cross sections of the PAH fluorescence in Figure 5. The ordinate axis position marks the midpoint of the drop array. Light line goes through drop; heavy line is midway between drops.

Figure 7 Image of scattered laser light from diesel drops passing through clouds of soot recorded at the second port. The soot material entrained in the drop wake indicates the high drop velocity with respect to the surrounding gases. Note that the drop acts as a lens and focuses laser light to a bright spot.