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LIQUID BEHAVIOR AT CRITICAL AND SUPERCRITICAL CONDITIONS

Huei-huang Chiu  
University of Illinois at Chicago

and

Klaus W. Gross  
NASA Marshall Space Flight Center

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ABSTRACT

At a JANNAF workshop the issue of fluids at and above the critical point was discussed to obtain a better understanding of similar conditions in combustion chambers of rocket engines. Invited experts from academic, industrial, and government institutions presented the most recent physical, numerical, and experimental advances. During the final discussion period it was agreed that (1) no analytical capability exists to simulate subject conditions; (2) mechanisms reflected by opalescence, the solubility of gases, other interfacial phenomena listed, and fluorescence diagnostics are new and important; (3) multicomponent mixtures, radiation, critical fluctuation, and other recorded ones pose unknown effects; (4) various identified analytical and experimental actions must be initiated in a mutually supporting sequence.

INTRODUCTION

A JANNAF workshop was held at the University of California, Irvine on September 6, 1989 to assess the State-of-the-Art of the critical and supercritical liquid behavior in liquid rocket thrust chambers.

The propellant injected into a combustion chamber which operates at a supercritical pressure may assume a sequence of states, starting with a subcritical one and ending at a final state which may be either subcritical, critical, or supercritical, depending on the initial droplet size and the thermodynamic condition. There is a genuine need to know the time-dependent states of the propellants, starting from the injection to complete combustion, because the anomalous behavior of thermodynamic and transport properties in the near critical region, and the disappearance of the liquid phase can significantly affect the spray process. It is surmised that those critical and supercritical behavior patterns have an impact on jet stability, dynamics of atomization, rates of mixing, heating, vaporization, ignition and combustion. Turbulent fluctuations are interconnected with the critical fluctuations in the near critical region, where the fluid exhibits anomalously larger isothermal compressibility and a reduced speed of sound.

In the critical and supercritical domain not only the state equation and thermodynamic functions are considerably different, but also the mechanisms and the rate of a chemical reaction, emission, absorption, and scattering of radiation are known to be different from that of an ideal gas.

All these unconventional thermodynamical characteristics cause various microscopic as well as macroscopic processes in the thrust chamber and thus ultimately affect the combustion performance and the stability behavior of a rocket engine.

GOAL

This workshop activity, oriented to examine the fluid behavior at critical and supercritical conditions, will ultimately contribute to the design and operational aspects of rocket thrust chambers, in particular to the:

1. Operational reliability, life cycle, and cost,
2. Thrust chamber performance characteristics,
3. Combustion process,
4. Combustion stability.

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## PARTICIPANTS

The workshop was conducted with invited participants from academia, industry, and government as indicated below:

### Academia:

Prof. Q. Brewster	Univ. Illinois-Urbana
Prof. H. Chiu	Univ. Illinois-Chicago
Prof. S. Elghobashi	Univ. California-Irvine
Prof. S. Jeng	Univ. Tennessee-Space Inst.
Prof. L. Melton	Univ. Texas-Dallas
Prof. S. Sadhal	Univ. Southern California
Prof. D. Santavicca	Penn State Univ.
Prof. M. Sichel	Univ. Michigan
Prof. W. Sirignano	Univ. California-Irvine
Prof. V. Yang	Penn State Univ.

### Experiment:

Prof. N. Chigier	Carnegie Mellon Univ.
Dr. G. Dobbs	United Techn. Res. Lab
Prof. S. Samuelsen	Univ. California-Irvine
Dr. W. Sanders	Sandia National Labs.

### Industry:

Dr. R. Jensen	Rocketdyne
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### Government:

Dr. J. Bellan	JPL
Mr. K. Gross	NASA/MSFC
Dr. J. Levine	AF/AL
Dr. L. Quinn	AF/AL/JANNAF Comb. Subcomm.
Dr. T. Shuen	NASA/LeRC/Sverdrup

### Workshop Organizers:

Prof. H. Chiu	Univ. Illinois-Chicago
Mr. K. Gross	NASA/MSFC

## OBJECTIVES

The objectives of the workshop were as follows:

1. Formulate a statement of the current simulation capability of fluids at critical and supercritical conditions.
2. Identify new knowledge addressing the fluid behavior in subject region.
3. Specify unknown physical characteristics affecting heat conduction, convection, and fluid mixing.
4. Recommend and prioritize technical topics in support of future research.

## WORKSHOP FORMAT

The workshop consisted of a series of presentations with a brief related discussion after each one. The presentation by the participants are listed below:

Flow Simulations in Combustion Chambers Operating at Supercritical Pressures	K. Gross
Review of Critical and Supercritical Phenomena in Liquid Propellant Rockets	H. Chiu
Atomization of Liquid Propellants	N. Chigier
Some Required Modifications of Droplet Theory	W. Sirignano
Multicomponent Droplet Vaporization at Near Critical Conditions	V. Yang
Operating Conditions in Supercritical Rocket Combustors and Modeling Suggestions	R. Jensen
The Effect of Swirl on the Group Vaporization and Combustion of Sprays	M. Sichel
Optical Diagnostics for Droplets in a Supercritical Environment	L. Melton

Following the presentations an open discussion was conducted in response to the workshop topics and objectives. The conclusions and recommendations reached by the participants are outlined below.

## 1. ASSESSMENT OF THE CURRENT SIMULATION CAPABILITY OF FLUIDS AT CRITICAL AND SUPERCRITICAL CONDITIONS

Current capabilities for the simulation of liquid propellant spray processes include analytical modelling and numerical simulation by Computational Fluid Dynamics (CFD) programs. Analytical efforts have been largely concerned with the prediction of (1) the behavior of a single droplet or a vapor puff at steady state vaporization or combustion, and (2) the transient evaluation of a droplet from a state of subcritical temperature to the terminal burning at supercritical condition. Some appropriate submodels describing the critical behavior have been adopted in these theoretical modelling attempts, however, many other considerations pertaining to the anomalous behavior of thermodynamic and transport properties of multicomponent mixtures have not been incorporated.

The state-of-the-art of the numerical simulation of spray processes in liquid rocket engines has been promoted and upgraded to account for phenomena such as droplet interfacial processes either in the presence or absence of collective interaction, multiphase turbulence, radiation, combustion, and the mutual interaction between those subprocesses. However, with the exception of a few numerical codes, the majority of existing CFD software has not been equipped with proper submodels, required for the predictions of the state of droplets; i.e. state of a droplet being either subcritical, critical, or supercritical. Needless to say, there is no spray code available, capable of predicting the critical and supercritical behavior and their impact on the overall combustion process, performance, and stability characteristics.

Existing analytical codes with limited spray combustion simulation and their basic features are listed in Table I.

Several comments were offered in connection with the current research in spray combustion.

- Theoretical and experimental research have been progressing at a somewhat mismatched pace. For example, a basic experiment such as the condition of a droplet in a supercritical environment should be carried out to establish the validity of the theoretical result. Unified experimental and theoretical research should be planned to ensure a balanced development.

- Research should emphasize the real system environment accounting for the factors of upstream conditions, type of propellants, and hardware design.

- Many results of actual test firings, e.g. Space Shuttle Main Engine (SSME) and other modern liquid rocket motors, are not available to the experts in universities and other research centers. It is suggested that the SSME test bed facility at NASA/SSME may be used to conduct relevant experiments, and that results be made available to the research community.

## 2. NEW KNOWLEDGE ADDRESSING THE FLUID BEHAVIOR IN SUBJECT REGION.

The new knowledge in the critical and supercritical regimes are fundamentally different from each other, and they are discussed discretely and separately in the following sections.

### ● Active and Inactive Critical Behavior

The overriding observation in the physics of the critical region is the divergence or disappearance of some thermodynamic properties, such as isothermal compressibility, the specific heat, surface tension, etc. Opalescence of the fluid around the critical point refers to the phenomenon of light scattering by the huge density fluctuation which renders a water milky and an opaque state at or very close to the critical temperature and pressure. Just slightly above or below the critical temperature by a fraction of a degree, water for example restores to its normal transparent state. This phenomenon, reflecting a new and unconventional microstructure of critical fluid, indicates that the conventional

physical model in this region is obsolete. Additionally, the vanishing surface tension and the latent heat of vaporization are responsible for the uncommon interfacial phenomena, such as the solubility of gas in the liquid. Those phenomena will significantly affect jet stability, atomization, deformation, vaporization, and combustion of droplets in a spray.

In contrast to some of those dramatic critical characteristics critical opalescence, disappearance of the discrete phase boundary, and other phenomena, caused by the singular behavior of some thermodynamic and transport properties, there is also a class of diverging thermodynamic properties that do not contribute to the critical phenomenon. For example, the divergence of the specific heat does not cause the divergence of enthalpy, and the vanishing mass diffusivity at the critical point does not completely impede the mass diffusion at a droplet interface.

These observations suggest that the critical behavior may be classified into two categories: "Active critical behavior" and "Inactive or degenerate critical behavior". The former refers to that behavior in which the unconventional physical phenomena may have observable macroscopic effects in the spray process. The latter, on the other hand, does not contribute at all to the abnormal observations on the macroscopic processes in the thrust chamber. The classification of the two types of critical behavior is somewhat complicated, and many experiments must be conducted to investigate these critical characteristics.

#### O Equation of State of a Multicomponent Mixture

Another area of new knowledge, linked with critical fluid, is the equation of state of a multicomponent mixture. Although it has been generally agreed that the critical behavior of a multicomponent mixture is basically a straight forward combination of the pure fluids, the thermodynamic description of the state of a mixture is considerably more complicated. In practically all cases the equation of state has been formulated after many trials and comparison of calculated mixture properties with experimental data. The construction of the engineer's equation of state for a mixture requires a number of parameters describing various types of intermolecular forces, molecular polarity, and the covolume effects of each of the particles. These parameters must be properly used to satisfy critical conditions that reflect basic thermodynamic characteristics, such as the vanishing of the first and higher order partial derivatives of the pressure with respect to volume at isothermal conditions. It also appears that the extensive use of the pressure-volume-concentration diagram and the mapping of a state in such a diagram is almost a mandatory practice in the determination of the evolutionary state of a propellant and the multicomponent reaction product mixture in a combustion chamber. This is particularly important in the subcritical region where cricondenbar (critical condensed bar = pressure) and maxcondenbar phenomena are likely to occur.

#### O Chemical Reaction in the Critical Region

The mechanisms and the rate of chemical reaction in the near critical region are virtually untouched by the research community of rocketry. The impact of intermolecular potential forces and the clustered molecular structure, as suggested by the optical opalescence, strongly hints that the kinetics of the reaction is significantly different from that of a dilute or an ideal gas.

#### O Solubility of Gases in Liquids

Although the abnormal increase in the solubility of a gas in a liquid has been observed, and the temperature dependence of the solubility of a gas or a gas mixture has been determined experimentally over the past decades, much of the data is of rather low quality and incomplete for the practical application to the liquid propellant thrust chambers. Various correlations of gas solubility in liquids have also been made, but with limited success. Furthermore, there has been no satisfactory theory for a gas-liquid solution. Existing theories, which are largely based on perturbed-hard-sphere theory, give gas solubility for a non-polar system, whereas the regular solution theory renders the solubility for a weakly polar system. Nevertheless, these theories are of limited use for engineering applications at this stage. It is apparent that an extensive knowledge of the physical mechanisms for the interfacial dissolving gas processes is required to develop a viable engineering model.

- Laws of Droplet and Droplet-Vapor Puff

The droplet processes of vaporization, combustion, and aerodynamic drag in the near critical region are complicated as a consequence of the vanishing surface tension and latent heat of vaporization, but increasing gas solubility. Furthermore, the initial droplet at subcritical temperature may transform into a droplet-vapor puff configuration, when the outermost part of the droplet becomes supercritical due to droplet heating. If the characteristic time of combustion is comparable to the one of state transition, a drop-vapor puff persists during its life time. However, when the characteristic burning time is longer than the state transition time, a vapor-puff law is required for the prediction of the characteristic burning time. Some of these vapor-puff models, which have been developed must be improved for implementation in the spray calculation.

- Interfacial Phenomena and Phase Equilibria

Interfacial processes in the near critical state are qualitatively and quantitatively affected by thermodynamic and transport properties, as well as phenomena linked with the solubility of a gas in a liquid and the critical fluctuation, caused by a large value of an isothermal compressibility, which make it difficult to establish stable gradients of velocity and temperature in the fluids. The interfacial problem in a multicomponent system is even more complex than in a pure fluid, because the phase equilibria of a fluid mixture requires appropriate theoretical models based on thermodynamics, physics, and chemistry to predict the interfacial process rate. However, the calculated properties of each mixture must be validated with reliable experimental data.

An additional concern in connection with the interfacial processes is the validity of the equilibrium postulation. This is particularly relevant, since the transport properties, thermal conductivities, and mass diffusivity are generally small so that the local thermodynamic equilibrium may not be warranted.

- Methodologies for Phase Transition, Thermodynamics, and Transport Properties in the Critical Region

It has been found that the strong scattering of light at the critical state, known as "critical opalescence", is caused by the wave length comparable to that of the characteristic correlation length of the density fluctuation of a cluster-like structure. The divergence of isothermal compressibility at the critical point is theoretically interrelated with this anomalously large correlation length. Thus, the phenomenon of critical opalescence can be used as a diagnostic tool for the identification of the critical transition of a pure fluid or multicomponent mixture. Furthermore, the intensity of the scattered light can be used to determine isothermal compressibility and other related thermodynamic properties. In addition to the method described above, the time dependent scattering of light has been used to determine the thermal conductivity, the sound absorption coefficient, and the speed of sound at the near critical point. In particular, the thermal conductivity and sound absorption coefficient are theoretically determined from the half-width of the Rayleigh and Brillouin components of the scattered light spectrum respectively.

- Fluorescent Diagnostic for a Droplet

Based on the photophysics and photochemistry of organic exciplexes (excited state complex) in hydrocarbon fuels, Melton and coworkers have developed a series of fluorescent diagnostic methods for the simultaneous measurement of the vapor and liquid phase temperatures. This optical thermometer uses the emission of an exciplex, produced by the reaction between an electronically excited monomer and a ground state molecule. The temperatures of the vapor and liquid phases are measured by the emission of the monomer and exciplex respectively.

Another noble optical diagnostic method for the observation of the internal circulation inside of a falling droplet, by addition of fluorescent dopants to the liquid, has been reported by Winter, Doffs and Melton.

Unfortunately, the method of exciplex emission can not be used for the phase selectivity needed to provide information about the critical behavior. Furthermore, the method of molecular fluorescence by the addition of dopants is not likely to produce incisive results.

### 3. UNKNOWN PHYSICAL CHARACTERISTICS AROUND THE CRITICAL POINT AFFECTING HEAT CONDUCTION, CONVECTION, AND FLUID MIXING

Historically, accurate physical characteristics in the near critical region were difficult to obtain, because of the critical instability. Although a large amount of experimental data exists to support theoretical predictions of the thermodynamic and transport properties, many of the properties of multicomponent mixtures, present in a typical liquid rocket chamber, are not well documented.

#### ● Properties at Critical and Supercritical Regions

Theoretical models for the prediction of the physical properties are still largely empirical. For example, a variety of functional relations between activity coefficients and concentrations, which are used in practical applications, are purely empirical, although some of these relations are upgraded by an improved understanding of the molecular interaction or the relative size of the molecules in their arrangement.

There is a need to establish a theoretical base for the prediction of transport properties of a multicomponent mixture for both critical and supercritical regions.

#### ● Critical-Supercritical Relationship

Many of the existing theories for critical and supercritical phenomena are largely confined to an isolated region, which is not obvious, because the equations for the two domains are mathematically different. Such fundamental relations are required for tracking the droplets in a spray combustion process.

#### ● Effect of Critical and Supercritical Behavior on various Processes

##### - Radiation under Critical and Supercritical Conditions

The critical opalescence is a well known example for the anomalous radiation behavior in a critical region. Little data and knowledge is available to describe the radiation phenomena in critical and supercritical realms where the radiation properties are different from those of the subcritical one. Such information is required for the determination of the radiative heat transfer rate.

##### - Turbulence in Critical and Supercritical Regions

The reduction of various transport properties, the singular behavior of thermodynamic properties, and the critical fluctuations are expected to change the nature of the hydrodynamic stability and turbulence, since the isothermal compressibility and the critical fluctuation will strongly interact with turbulence. The mechanisms of turbulent transport processes and their impact on local momentum, mass, and heat transfer must be understood to simulate the overall spray process.

### 4. RECOMMEND AND PRIORITIZE TECHNICAL TOPICS IN SUPPORT OF FUTURE ACTIVITIES

Studies are recommended for near critical and supercritical conditions to obtain (1) measurements of fundamental properties, and (2) to characterize analytically the injection of a droplet into a combustion chamber.

#### ● Measurements of Fundamental Properties at Near Critical and Supercritical Conditions

The basic thermodynamic and transport properties of selected fluids and mixtures at critical and supercritical conditions are required for the calculation of the combustion flow field in a thrust chamber. This data and relevant thermochemical information are needed for the determination of the equation of state, critical pressure, and temperature for prescribed species concentrations to predict the global flow field. The experiments must be conducted to assist in the validation of the results from theoretical models and for establishing empirical correlations in the regions of practical interest in a liquid rocket chamber environment.

- Analytical Characterization of Critical and Supercritical Vaporization and Combustion of a Droplet

A detailed time dependent model, simulating the behavior of a liquid droplet in a critical/supercritical environment, should be initiated to examine the effects of the anomalous behavior during vaporization and combustion. Experimental data must be used to validate the results from advanced theoretical models for droplet vaporization and a vapor-puff behavior. The departure of the vaporization rate from the classical theory, based on subcritical conditions, should be assessed to establish a correction factor for the vaporization rate. Additionally, the transition from a subcritical to critical and supercritical state needs to be examined.

- Assessment of Time and Spatial Scales

The anomalous behavior of transport properties introduces multi-scale problems in the near critical region. Furthermore, the characteristic length and time associated with the critical fluctuation must be known to assess their impact on the local flow field characteristics. The time and spatial scales are used for the determination of the major non-dimensional flow parameters, such as Reynolds, Prandtl, Lewis, and Schmidt numbers, to estimate the relative importance of various subprocesses. Theoretical models of droplet interfacial processes, drag, vaporization, and combustion, accounting for the critical and supercritical behavior, are needed for the prediction of spray combustion in a liquid rocket combustion chamber.

- A Criterion to determine the State of Propellant Droplets

A Comprehensive criterion that identifies the state of a droplet should be formulated to facilitate the calculation of the droplet change rate. This quantitative criterion must be encoded in a spray CFD code for the evaluation of the complete spray process.

- Development of Droplet Laws

Theoretical droplet laws containing droplet drag, heating, vaporization, and combustion, accounting for the gas solubility, diminishing surface tension, and disappearing latent heat of vaporization are needed for the numerical prediction of sprays. These laws must take into account the effects of (1) short-range collective interaction and long-range group phenomena, (2) convective motion of the gas relative to a droplet, and (3) transition between thermodynamic states, i.e. subcritical to critical to supercritical transition. Additionally, the variations in fluid, thermodynamic, and transport properties should be incorporated in the spray calculation.

- Grand Computational fluid Dynamics Code

A comprehensive spray CFD code, capable of numerically predicting the entire spray flow field, must be developed for the performance analysis of a rocket thrust chamber and the simulation of combustion instability. The code must provide the distributions of the major flow variables and the identification of the subcritical, critical, and supercritical regions.

### CONCLUSIONS

The workshop served to identify the practical significance of the critical and supercritical fluid behavior in liquid propellant rocket engines. Substantial fundamental research effort is being conducted to determine the effects of anomalous fluid behavior on the spray processes in these regions. However, there exists also a considerable scientific and engineering gap in the fundamental knowledge of the atomization, interfacial, and vapor-puff processes.

New optical diagnostic methods, based on the critical opalescence, appear to be a potential tool for the understanding of the behavior of the thermodynamic and transport properties in these regions. This technique should be further exploited to develop reliable diagnostic tools. Fundamental and applied research, focused on the single droplet and a spray system, operating in subject regions, are needed to establish viable procedures for the prediction of the performance and stability characteristics of modern liquid propellant engines. The effort will undoubtedly promote the state-of-the-art of the aerodynamic and combustion

characteristics and will serve to improve basic design, system reliability, and the development of low cost engines for future space propulsion systems.

A workshop summary, containing this report and the material used by some participants during their presentations, has been prepared and can be provided upon request by K. Gross.

Table I

Program or Developer	Subcritical Critical Supercritical	Eulerian or Lagrangian	Phase
LHF	C, Sub	E-E	Lq, G
W.Sirignano	Sub	E-L	Lq, G
ARICC	Sub	E-L	Lq, G
KIVA	Sub	E-L	Lq, G
R. Reitz	Sub	E-L	Lq, G
SSF	Sub	E-L	Lq, G
REFLEQS	Sub	E-L	Lq, G
GEMCHIP II	Sub	E-E	Lq, G
GEMCHIP III	Sub	E-E	Lq, Lq, G

Nomenclature:

Sub = Subcritical, C = Critical, Sup = Supercritical  
 E = Eulerian, L = Lagrangian, Lq = Liquid Phase  
 G = Gas Phase