
DOE/ER/13902-6

# THERMOPHYSICAL PROPERTIES OF SUPERCRITICAL FLUIDS AND FLUID MIXTURES

Technical Report

December 15, 1988 - December 14, 1994

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August 1998

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER GRANT NUMBER DE-FG05-88ER-13902

Institute for
Physical Science and Technology

# DISCLAIMER

## I. INTRODUCTION

This report covers research supported by Grant No. DE-FG05-88ER-13902 during the period from December 15, 1988 till December 14, 1994.

A preliminary report covering the research accomplished under DE-FG05-88ER-13902 was incorporatd into a renewal proposal "Thermophysical Properties of Fluids and Fluid Mixtures" submitted to the DOE Office of Basic Energy Sciences in 1994. Upon request from DOE this report completes the account of all research performed under this grant.

In Section II we briefly state the goal of the research. The research accomplishments are described in Section III. A list of publications completed under DE-FG05-88ER-13902 is presented in Section IV.

## II. RESEARCH GOAL

This research is concerned with the development of quantitative scientific descriptions of the thermodynamic and transport properties of supercritical and subcritical fluids and fluid mixtures. It is well known that the thermophysical properties of fluids and fluid mixtures exhibit singular behavior at critical points. Asymptotically close to critical points the thermophysical properties satisfy scaling laws with universal critical exponents and universal scaling functions. However, the range of validity of these asymptotic scaling laws is very small.

The singular critical behavior of the thermophysical properties is caused by the presence of fluctuations in the order parameter associated with critical-point phase transitions. In one-component fluids near the vapor-liquid critical point the critical fluctuations are fluctuations in the density. More generally, in fluid mixtures the critical fluctuations involve both density and concentration fluctuations.

It has now been well established that the range of temperatures and densities where various thermophysical properties are affected is quite large. The reason is that the correlation length associated with the critical fluctuations exceeds the short-range molecular interaction range in a sizeable part of the phase diagram of fluids and fluid mixtures. Thus to obtain a scientific description of the actual behavior of the thermophysical

properties of fluids and fluid mixtures it is necessary to develop a theory of the global behavior of the thermophysical properties resulting from the critical fluctuations including both nonasymptotic critical behavior and crossover to regular behavior far away from critical points.

## III. RESEARCH ACCOMPLISHMENTS

### 3.1 Thermodynamic properties of one-component fluids

We have developed a theory for the global critical behavior of the free energy of fluids that includes the crossover from Ising-like singular behavior asymptotically close to the critical point to regular behavior far away from the critical point [3,5-8,10,12,18,20,21,27,33]. This theory starts from a classical Landau expansion for the Helmholtz free-energy density which is then modified to account for the effects of critical fluctuations by applying results from the renormalization-group theory of critical phenomena. When the theory is applied to a two-term Landau expansion one obtains an equation of state that exhibits the crossover from asymptotic Ising-like singular behavior to asymptotic mean-field behavior [20].

It is of specific interest to consider the crossover behavior of the susceptibility $\chi$ which for one-component fluids may be identified with $(\partial\rho/\partial\mu)_T$, where $\rho$ is the density and $\mu$ the chemical potential. The crossover behavior of the susceptibility $\chi$ can be represented by a universal function of the temperature difference from the critical temperature when the latter is scaled with the Ginzburg number [20]. This crossover behavior includes an effective exponent $\gamma$ varying from the Ising-like value 1.24 at the critical point to the classical value 1.00 away from the critical point. Such a crossover behavior has been observed experimentally in some polymer systems. It has recently been shown that our theory does account for the experimentally observed crossover behavior of the susceptibility of polymer blends.

A crossover theory based on a two-term Landau expansion is inadequate to give a quantitative representation of the behavior of the thermodynamic properties of normal fluids. The reason is that the effects of the critical fluctuations remain important until so far away from the critical point that an asymptotic mean-field theory will never become applicable. Hence, we have also developed a theory of the crossover behavior

of the Helmholtz free-energy to nonasymptotic mean-field behavior by retaining also higher-order terms in the Landau expansion. In practice we have found a six-term Landau expansion to be adequate [5]. We have applied this theory to represent the thermodynamic properties of a number of fluids in the critical region, namely carbon dioxide [5], steam [5,36], ethane [5,21] and methane [15]. It is also possible to use the theory to calculate the thermodynamic properties in the critical region from a restricted amount of experimental information as we have demonstrated for the alternative refrigerant R134a [6,26].

Recently, we have made some modifications in our crossover theory which have increased its applicability to even a larger range of temperatures and densities. This improvement has been documented in a Ph.D. thesis [27]. We have also made some modifications in a semi-empirical formalism developed at the Oil and Gas Research Institute of the Russian Academy of Sciences leading to basically equivalent results [25].

The theory for the global critical behavior of the Helmholtz free energy amounts to the application of a transformation to a classical Landau expansion. We have also initiated an investigation whether a similar transformation can be applied to closed-form equations of state like the generalized van der Waals equations often used for chemical-engineering applications. We have formulated such a transformation and applied it to a Carnahan-Starling-de Santis equation of state [31]. The transformed equation incorporates the universal scaling-law behavior asymptotically close to the critical point, while at the same time approaching the universal ideal-gas behavior in the low-density limit.

3.2 Thermodynamic properties of fluid mixtures

We have extended the theory of the crossover behavior of the Helmholtz free energy to binary fluid mixtures [24,27]. This extension is based on the isomorphism principle. In simple words this principle amounts to a one-fluid mixture model in field space. If the mixture is considered not at constant concentration but at a constant value of a properly chosen field variable $\zeta$, the critical contributions to the equation of state become isomorphic with those in the equations of one-component fluids. This principle has been used successfully to represent thermodynamic data of fluid mixtures at vapor-liquid equilibrium.

Specifically, we have applied this crossover theory to represent thermodynamic-property data of mixtures of carbon dioxide and ethane [24,27]. In the case of mixtures we need an accurate representation of the critical parameters as a function of the composition and we examined the available experimental data for the purpose [22]. In our initial application we encountered some complications which seemed to indicate inconsistencies between different data sets [24]. If a better representation of the critical parameters as a function of the concentration is adopted, the crossover theory does describe the thermodynamic-property data of carbon dioxide + ethane mixtures in the same range of temperatures and densities as for the pure fluid components [27]. A good representation of vapor-liquid equilibrium data is also obtained [27]. Most recently, we have extended the theory to incorporate crossover between vapor-liquid and consolute critical phenomena in fluid mixtures [37].

3.3 Transport properties of one-component fluids

The thermal conductivity exhibits a critical enhancement in a large range of temperatures and densities. We have also developed equations to account for the crossover behavior of the thermal conductivity [2,30,38]. These equations have been derived on the basis of the mode-coupling theory of the dynamics of long-range fluctuations [38]. These equations have been adopted by several investigators to represent the thermal conductivity of fluids. We have used these equations to represent the transport properties of ethane [4,28,29] argon [34] and R134a [26,32]. The tables that we have prepared for the transport properties of R134a [26] will be included in the Bulletin of the International Engineering Association Annex 18, which effectively means that they will become internationally recommended tables for R134a.

In contrast to that of the thermal conductivity the critical behavior of the viscosity is weak and subtle. We have made some improvements in our equations so as to obtain a more accurate description of the critical behavior of the viscosity [30]. With this improvement the theoretical equations are in good agreement with the most accurate viscosity data near the critical point, namely those obtained by Berg and Moldover for carbon dioxide [30].

3.4 Transport properties of fluid mixtures

Most recently we have also succeeded in extending the theory of the global critical behavior of the transport properties to binary mixtures [30,35]. In parallel to the development of this theory, we have measured the thermal conductivity of mixtures of carbon dioxide and ethane with a parallel-plate apparatus especially suited for the measurement of the thermal conductivity of fluids in the critical region [11,16,19]. With the new crossover equations for the transport properties of mixtures we have been able to obtain a good description of these experimental thermal conductivities for the carbon-dioxide + ethane system [30]. Moreover, from these equations we are also able to predict the behavior of other transport properties of this mixture, like the thermal-diffusion ratio [30].

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