Chapter 1
Thermal Effects in Near-Critical Fluids:
Piston Effect and Related Phenomena

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ABSTRACT

This chapter addresses the very particular thermal behavior that supercritical fluids exhibit when nearing their critical point. In this region, supercritical fluids exhibit strong anomalies in their thermodynamic and transport properties. Pressure change associated to a temperature variation leads to a nearly isentropic thermalization of the fluid, the "piston effect," which leads to a paradoxical "critical speeding-up." Bulk fluid temperature is uniform, and temperature gradients are confined in thermal boundary layers, making the bulk fluid a thermal short-circuit. It follows very particular behavior, as dynamic heat pipes or heat going seemingly backward, in apparent contradiction with the second principle of thermodynamics. Under an acceleration field, thermal convection occurs only in the boundary layers, which paradoxically can enhance the fluid stability or even cool the fluid after a heat pulse. These effects can deeply modify the supercritical fluids thermal behavior in space and energy activities, giving to these effects socio-economic relevance.

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INTRODUCTION

Classically, one considers that fluid can be thermalized by three different modes: radiation (where heat is exchanged by emission and absorption of electro-magnetic waves), diffusion (as in a solid), and convection by flow motion. In the following, we focus on diffusion and convection and see that in compressible fluids like supercritical fluids nearing their critical point (near supercritical fluids), another thermalization effect, the « Piston effect» (PE), where a thermal boundary layer expands and adiabatically heats the fluid, can be of high importance. This is especially true in space weightlessness where convection no more occurs and where the PE has been observed the first time. On earth, this PE, although in competition with convection to thermalize near supercritical fluids, eventually reveals to be the main process responsible of their thermalization. In addition, this thermo-compressible effect leads to very peculiar and paradoxical phenomena in heat transport and thermalization, seemingly in disagreement with the 2nd thermodynamics principle.

These effects can modify in a significant manner the thermo-mechanical response of supercritical fluids when they reach the (immediate or not) vicinity of their critical point. This is particularly the case for supercritical fluid used in the space industry and propulsion under weightlessness. For instance, the supercritical water oxidation (SCWO) process was one among the selected processes to treat the waste materials involved in the life support for the space exploration (see Major, 2014; Phillips, 2014). Similarly, near-critical fluids can be used as relevant models (Nikolayev, 2015) to study the boiling crisis dynamics in high power thermal plants including nuclear plants and the analysis of safety risks (Juhaszl et al., 2009).

GENERAL BACKGROUND

Supercritical fluids, that is, fluids at pressure and temperature above their critical point (CP) coordinates, exhibit particular properties (large density, low viscosity, large mass diffusivity), which make them intermediate between liquids and gases. It was indeed well-recognized from the end of the 90's that the fine pressure/temperature control of the supercritical conditions is very appealing to the industry as an easy mean to tune their non-polluting solvatation power and host the chemical reaction rates with high yield efficiency (see for example Noyori, R., 1999 and related papers in the same special issue). Fluids in such supercritical conditions are now mainly used to open new routes in green synthesis of innovative materials (Adschiri et al., 2015; Dumas et al., 2016) or in hydrothermal biomass conversion processes (Kruse & Dahmen, 2015).

In addition, the fact that temperature is large increases the yield of thermo-mechanical processes in *boiling water, steam or* molten salt reactors. Under reduced gravity, the storage of cryogenic propellants is sometimes performed in their supercritical conditions to avoid a non-controlled two-phase distribution However, when temperature and pressure approach the CP values, such fluids show strong anomalies in a number of static and dynamical properties. In particular, isothermal compressibility, thermal expansion and specific heats at constant pressure and volume can become extremely large. Dynamical properties can also be much affected. The so-called "critical slowing down" corresponds to a strong decrease of thermal diffusivity while, in contrast, heat conductivity and specific heat diverge. In the vicinity of the critical point temperature and pressure, such fluids are called « near critical" or "near supercritical ». We address below the main properties of such near supercritical fluids.

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