Supercritical Fluid Near the Critical Point: The Piston Effect

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Abstract

This essay describes thermalization at the critical point while under the effects of microgravity. In particular it covers the piston effect discovered in absence of Earth's gravity and the subsequent research this effect initiated.

1 Introduction

A pressure vs. temperature phase diagram is often a student's first encounter with the phase known as a supercritical fluid. Some students also directly observe the transformation of a liquid-gas system into its supercritical state through the disappearance of the meniscus boundary which acts as an indicator of the boundary between the bulk liquid and the bulk gas states. Such a common academic exercise belies the difficulties in understanding the many properties of this classically observed phenomenon.

Three processes of thermalization, how a system attains thermal equilibrium, have been understood for many decades. These phenomena are known as radiation, diffusion, and convection. Each of the processes listed have been applied to physical observations in order to aid in understanding phenomena as varied as binary alloy formation, tectonic plate dynamics, and solar system evolution. However, radiation is a negligible process for the temperatures and pressures under consideration here.

Yet, despite this understanding, only two decades ago scientists discovered a fourth method of thermalization. This method, termed the piston effect, has several reasons for having eluded scientific discovery for so long. After an instructional illustration, the following pages describe the discovery and subsequent explanation of the piston effect. Practical limitations of observing this effect as well as the theorized and realized applications then follow. Finally, current and future work related to the piston effect is discussed.

2 The Piston Effect

The piston effect is best illustrated near the critical point of a fluid in the supercritical bulk phase (e.g. CO_2 near 305K and 73 atm). Supercritical fluids have a unique combination of liquid and gas properties. These include high density and high solubility similar to liquids, as well as very low viscosity and high mass diffusivity similar to gases. In addition, since a supercritical fluid can be tuned to liquid or solid without a phase transition, any of the above properties can be adjusted to give the fluid more gas- or liquid-like qualities.

If the fluid is brought close to the critical point it gains additional properties such as high compressibility and vanishing diffusivity. It is these two properties along with a vanishing gravitational force which allow the piston effect to become the dominant mode of thermalization. To see this, suppose you have a thermally isolated container of liquid in the supercritical state near its critical point (Figure 1). After allowing this fluid to come to thermal equilibrium, apply a heat pulse to the fluid on one side of the container. Due to the high compressibility and vanishing diffusivity, the fluid close to the heated side will expand without heating the bulk of the fluid. This expansion creates a longitudinal density wave which propagates through the bulk fluid at the speed of sound. The high density, highly compressible supercritical fluid converts some of this kinetic energy into thermal energy, heating the bulk uniformly each time the wave passes. This effect would be negligible if the other thermalization methods were not suppressed. Near the critical point diffusion time scales diverge, and in the absence of gravity convection cannot take place. The dominant thermalization method is then the conversion of a density wave into uniform bulk heating. Since the time for a sound wave to traverse a small (cm) sample is much shorter (sec) than the time for the sample to come to equilibrium through diffusion (hours-months), this process can be considered adiabatic. Conversely, if one wall is cooled the fluid near it will contract and cause adiabatic cooling throughout the bulk fluid. This resembles the effect a piston has on a compressed gas in basic thermodynamics, hence the term piston effect.

3 Discovery

In 1985 Spacelab mission D-1 conducted several experiments in microgravity [2]. Among these was a measurement of the heat capacity (at constant volume) at the critical point of SF_6. Performing this experiment on Earth is difficult for many reasons. Diverging compressibility causes large density gradients, which ensures that a sample is only very near the critical point in a thin layer. The necessity for large volume samples in calorimeter measurements therefore makes this impractical. Additionally, a system near the critical point under gravity acquires a divergent Rayleigh number, leading to convection dominated dynamics even under relatively small temperature gradients. Performing the same experiments in microgravity greatly reduces these issues.

Prior to this experiment, scientists theorized that a system near the crit-

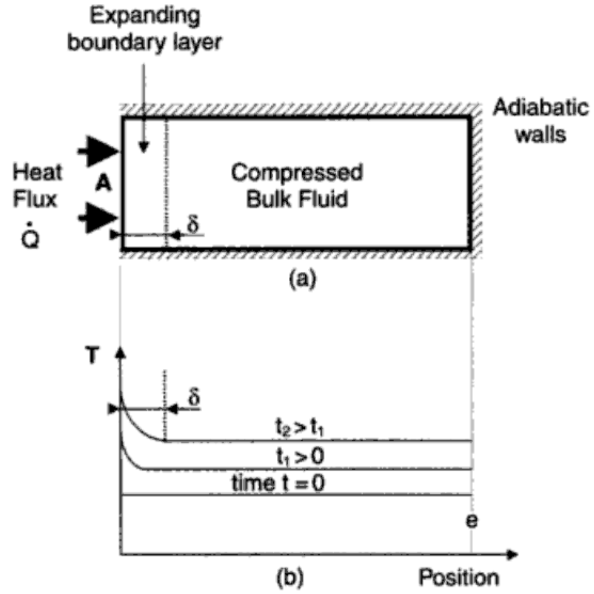

Figure 1 – The piston effect from Monti [1]. On the left a heated boundary layer of size δ quickly expands (a). This compresses the bulk fluid resulting in large temperature gradients at the boudary and uniform heating in the bulk (b).

ical point exhibits a relaxation time which increases as gravity is decreased. This effect is directly related to the diverging diffusion time for particles in this critical, microgravity state. With convection suppressed as well under low gravity conditions thermal equilibrium was expected to occur only at larger time scales. As described in the previous section there is, instead, a decrease in the relaxation time, but during the 1980's scientists were unaware of this fact. Straub and Nitsche [2] show a graph (Figure 2) comparing average heat capacity $\bar{c}_v$ measurements on Earth to measurements in microgravity. The microgravity results deviated greatly from previous theoretical models. After carefully checking the equipment for errors on Earth the authors studied the calorimeter data to determine relaxation times. They found that thermalization occurred with a relatively short relaxation time, but diffusion still had the expected longer relaxation. Concluding that the system underwent what is now reffered to as critical speeding up, many scientists were initially skeptical of this result.

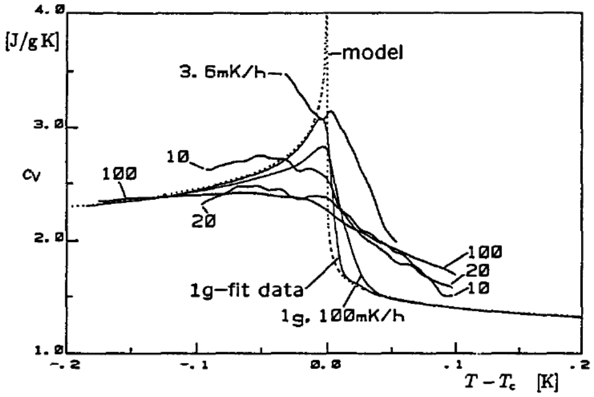

Figure 2 – $\bar{c}_v$ measurements on Earth (denoted by 1g) and in microgravity. Note the Earth-based curves approach closer to the theoretical divergence than the D-1 Spacelab experiment curves.

4 Early Difficulties

In addition to the many critical point and nonzero gravity phenomena which serve to suppress the piston effect, practical limitations also led to its relatively late discovery. The most apparent limitation is technological: the requirement of space or high altitude flight. Without such technology no known experiment can probe low gravity systems. Associated with this advanced technology are the high costs of each mission. Microgravity experiments also suffer from reduced durations in comparison to experiments conducted on Earth. Straub and Nitsche [2] report the D-1 Spacelab mission allowed approximately 100 hours for a typical experiment, but a fluid near the critical point suffers from diverging density equilibration times, leading to inhomogeneities that are subsequently ubiquitous throughout experiments of this nature. Given these constraints, one can then understand why the piston effect was not discovered until long after the other three thermalization methods.

5 Theory

By 1989, Onuki *et al.* [3] proposed an adiabatic heating method which could account for fast thermalization. Other groups (e.g. [4],[5]) independently produced similar models accounting for this thermalization phenomenon. Shortly after the piston model was proposed, Zappoli *et al.* [5] confirmed the accuracy of the model numerically (Figure 3).

Garrabos *et al.* [6] mention two major time scales and their relation as follows. Denote t_0 as the time to transfer energy from the boundary layer to the bulk fluid E_b. This initial energy transfer occurs due to the expansion of the boundary layer, which compresses the bulk fluid. Assuming $\delta \ll L$, where L is the length of the sample and δ is the width of the expanded boundary layer, the temperature T_b will change as $\Delta T_b \approx \frac{E_b c_v}{L}$ with c_v the specific heat capacity at constant volume. Equilibrium temperature requires the boundary layer temperature to reach the bulk temperature value, giving $\Delta T_b \approx \frac{E_{bdry} c_p}{\delta}$ where c_p is used since the boundary layer has expanded but is subject to nearly constant pressure in proximity to the heat bath. Equating the two temperature changes we find

$$\begin{aligned} \frac{\frac{E_b}{L}}{c_v} &\approx \frac{\frac{E_{bdry}}{\delta}}{c_p} \\ \Rightarrow \delta &\approx \frac{L}{\gamma_0} \end{aligned}$$

where $\gamma_0 = \frac{c_p}{c_v}$. Onuki and Ferrell [7] found an exact result of $\delta = \frac{L}{\gamma_0 - 1}$. Finally writing $t_0 = \frac{\delta^2}{D_T}$ and $t_D = \frac{L^2}{D_T}$, where t_D is the diffusion time and D_T is the thermal diffusivity in the fluid, we find our expected relation to be

$$t_0 = \frac{t_D}{(\gamma_0 - 1)^2}.$$

Since $\gamma_0 \to \infty$ as the fluid approaches the critical point we see that $t_0 \to 0$ obtaining what is termed the 'critical speeding up' effect. Note that the time it takes for an acoustic wave to propagate across the sample forms a lower bound on t_0.

Direct experimental evidence of the piston effect was published in 1990 (Figure 4). Boukari *et al.* [8] present a set of compressible fluid equations accurately describing the critical system in Earth's gravity as well as in microgravity. In addition, the experimental results reveal that the adiabatic heating process akes place in a time on the order of the acoustic time scale, which decreases as the system approaches the critical temperature.

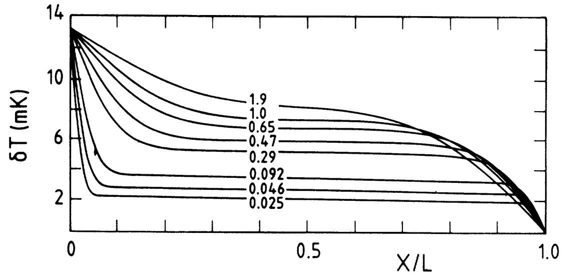

Figure 3 – Each curve represents the temperature distribution accross a model 1-D system at a point in time after application of a heat pulse. Note the approach to equilibrium is on the order of 1 sec. This time is much shorter than diffusion equilibrium time in microgravity near the critical point.

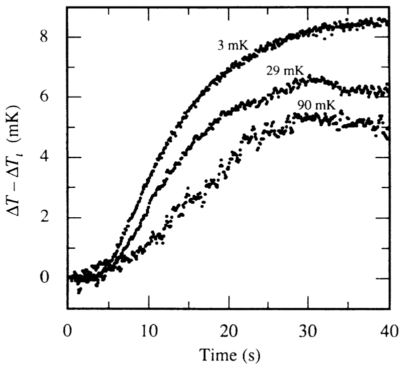

Figure 4 – Direct experimental evidence for critical speeding up. The temperature change as a function of time at 3 different temperatures. Value along the curve denotes difference between trial temperature and critical point. The time for the sample to come closer to equilibrium decreases as the sample is brought closer to T_c.

6 Development at g=1

Initial experiments required a microgravity environment to allow the piston effect to dominate the process of thermalization. In 1998 Zappoli [9] presented numerical calculations arguing that under Earth's gravity the piston effect still plays a non-negligible role regarding thermalization near the critical point. In this paper, a simple 2D cell model heated from the bottom of the cell shows the characteristic fast, uniform temperature increase of the piston effect (Figure 5). Once the convective flow brings the heated fluid into contact with the upper wall, the cooler wall acts to contract the uppermost layers of the heated fluid. This proceeds to initiate the cooling piston effect, which competes with the heating piston effect already present in the bulk fluid. The two adiabatic density waves, formed from the same heated fluid changing density, then proceed to cancel each other. The result shows that a computational model incorporating gravity leads to an observable piston effect regardless of the presence of convection. Not only is the piston effect present at Earth's gravity, but it is self canceling on the order of the time it takes for convection to transport the heated fluid across the cell vertically.

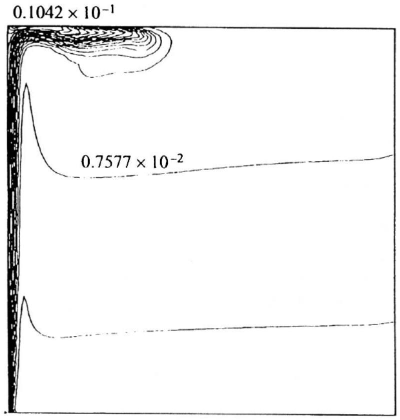

Figure 5 – A temperature contour plot (with values given in Kelvin) from a 2D computational model. The two lines in the bulk indicate a somewhat uniform temperature increase throughout the fluid. This graph was taken 4.5 sec after allowing a 1mK temperature increase at the left boundary. Convection is noticable, but clearly not responsible for the uniform temperature increase.

7 Resultant Directions

There are several direct results of the discovery and subsequent explanation of the piston effect. The first concerns the energy transfer efficiency of the effect. It is clear (Figure 4) that temperature equilibration is very efficient, resulting in near equilibrium bulk temperatures on time scales much shorter than the diffusion rate of the fluid. In contrast, calculations of the energy transfer efficiency give a value around $\xi = 1/7$ where $\xi = \frac{\Delta E(t)}{E(t)}$ is the amount of energy added to the bulk over the total energy added to the system [6], which seems to contradict the fast temperature change. This drastic difference between temperature equilibrium and energy transfer efficiencies can be readily explained through the state of the fluid. With the supercritical fluid near the critical point, its internal energy is very sensitive to density changes. Since the formation of the heated pocket creates a small particle flux into the bulk the *internal* energy rises appropriately to give the observed temperature increase.

A second development addresses a phenomenon known as local overheating. The possibility of localized regions of the bulk fluid gaining a temperature significantly above the equilibrium temperature which the sample can obtain would seem to contradict the second law of thermodynamics at first glance. The resolution of this apparent paradox lies in the mechanical nature of the piston effect. As is indicated by the name of the effect itself, the piston effect is a mechanical process. The fluid is subject to mechanical equilibrium conditions, which can, at sufficiently inhomogeneous density profiles, lead to local overheating and cooling in portions of the bulk. Local overheating was observed in two-phase fluids as early as 1990 [7], and by 1999 an experiment was conducted specifically to observe this effect [10]. The results clearly indicate overheating in the bulk sample (Figure 6).

8 Future Outlook

Recent studies of the piston effect in both experiment and the resultant numerical simulations offer a high resolution view of the piston effect (Figure 7). The higher resolution measurements have allowed for the study of the density wave shape and speed. Miura *et al.* [11] note that relations between viscosity and heat transport need clarification. Numerical studies by Zhang

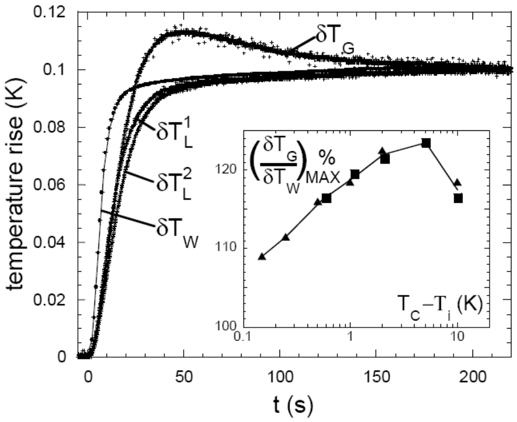

Figure 6 – Temperature change as a function of time at the cell wall δT_w, the two liquid phases δT_L^1, δT_L^2, and the gas δT_G. The experiment heats the outside walls of two liquid SF_6 layers which contain a gas layer between them. The heat pulse added 100mK to the boundary layers. By 50 sec the gas layer has been heated above the equilibrium value nearly 15mK. The inset shows that the gas layer can exceed the wall equilibrium temperature by up to 123%

et al. [12] indicate that calculations tend to be carried out using overly simplified boundary conditions. More detailed damping measurements in the future would help confirm the models governing dynamics of the piston effect. A careful study could include, for example, system walls of finite heat capacity and thermal conductivity.

9 Conclusions

The piston effect, theorized in 1989 and unambiguously observed in 1990, is a distinct, fourth method of thermalization typically observed in supercritical fluids near the critical point. Discovery of this effect required a suitable microgravity environment in order to suppress the convection present in density stratified samples on Earth. This phenomenon contains an unusual set of properties including bulk adiabatic temperature equilibration, local overheating, and low thermal energy transfer efficiency. These effects can be understood through the mechanical nature of this thermalization method. Although the piston effect is described using classical fluid theory, its discov-

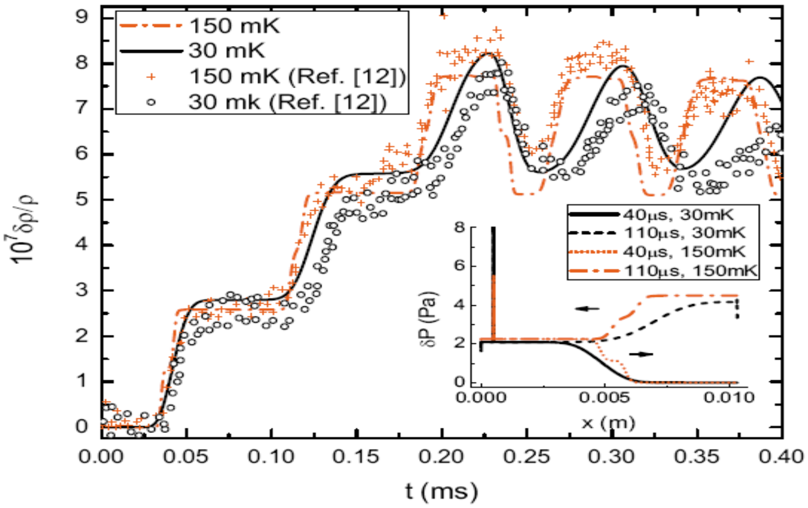

Figure 7 – Precise measurements of density variation with time at the center of the sample for experiments and computations. Lines and dots correspond to computations and experiments respectively. The inset shows pressure gradients throughout the sample at various times with arrows indicating wave propagation in the sample before and after acoustic wave reflection at the sample boundary.

ery was relatively recent, and several recent articles have been published attempting to accurately describe its effects and implications for thermalization dynamics. This effect is part of an active field of microgravity experiments with prospects of continued research both under microgravity conditions as well as within Earth's gravity.

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